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DOTTORATO DI RICERCA IN SCIENZE DELLA TERRA
XXIII CICLO

Enviromental geochemestry study to define baseline (background) values of toxic elements in an high-urbanized and industrialized area (Comune di Casoria)

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1 Introduction

The human activities impact on the environmental conditions is the central discussion of the scientific studies that deal the pollution of the soils and water.

In the last years environmental problems in the Campania region becomes on worldwide attention for different kind of reasons. The illegal disposal of domestic and other potential wastes and the burning of trash piles have raised concerns in the Naples and Caserta provincial areas that people who lives there could be at risk of unacceptable health consequences from exposure to the trash and related contaminants. These contaminants may be present continuously or at intermittent times in air, water, and soil, depending on the nature of the contaminants.

1.1 Aims and phases of the research

This study presents the results of the environmental study on the Comune di Casoria area, Italy.

In the last years Casoria, that still remains one of the higher urbanized place near Naples, was involved in the waste emergency, which, adds to high vehicular traffic and present and past industrial contamination, makes this area the perfect target to environmental geochemistry study.

The aim of this environmental study is to characterize, geochemically and isotopically, a land on which no previous scientific work were realized, in order to better understand: the degree of the contamination, the sources that have caused it, and improve the knowledge about the pathways for contaminants diffusion throughout the environment.

The whole study developed in two main and well distinct phases:

- the first has been a preparatory phase in which, through different media sampling and related data elaboration, has been possible to select the areas where concentrate the Pb isotopic studies;
- the second part of the research is the one focused on the Pb isotopes analysis and on the interpretation of the obtained data.

In the first part of the study, a homogeneous sampling of 126 surface soils (5-20 cm), 50 samples from 5 soil profiles (0-1 m), 5 tap water, was carried out.

The whole field activity was realized on the basis of a sampling grid; FOREGS sampling procedures (Plant et al., 1996; Salminen et al., 1998) have been strictly followed during all the steps.

After their preparation in the Laboratories of the University of Naples, surface soils samples have been analysed to determine the concentrations of 50 elements, by using the ICP-MS technique. Obtained data have, then, been statistically and cartographically processed.

Surface soil samples, soil profiles,and tap water samples have been prepared and analysed during the last year at the USGS Laboratories in Reston (VA, USA) in collaboration with Dr. Robert Ayuso and his staff to detect isotopic ratio of Comune di Casoria samples.

1.2 Use of Pb isotopes in environmental studies

During the last 60-80 years, the rapid increase and development of human activities such as industrial plants and intensive farming, has brought about great changes into the environment, and has introduced new risks and hazards for nature and human beings. In order to characterize the affected environment, the use of tracers and environmental indicators, has been a widely diffused and effective operational tool.

Many studies conducted since the 70-80's in different countries and on different analyzed media, have all led to the opinion that Pb isotopes are some of the best tracers to be used for environmental purposes.

Lead is one of the most toxic and harmful element for plants, animals and humans. Its presence into the environment, can be related to both natural and anthropic origin, the first deriving from the Pb-rich rock

weathering, and the last mainly deriving from the combustion of gasoline and from industrial smelting. These anthropic activities introduce into the environment very large amounts of Pb; according to some scientific works (Shirahata et al., 1980; Flegal et al., 1989; Nriagu, 1989) its anthropogenic pollution is estimated to account for 96-99% of the total atmospheric Pb deposition. Air is the chief way through which

anthropogenic Pb is released and widespread; activities such as smelting, waste incineration, car exhausts and mining, introduce it in the atmosphere as airborne and particulate. Through air circulation, Pb can be transported even for long distances and, then, be deposited on soils. Once in soils, it can be absorbed by plants and enter in the food chain through the ingestion of contaminated plants by animals, thus influencing the entire biological cycle. In soils, Pb mainly concentrates in the surface horizon; nevertheless in some cases (Sterckeman et al., 2000; Denaix et al., 2001; Citeau et al., 2003; Jensen et al., 1999) its downward migration may occur and anthropogenic Pb can reach the groundwaters. This phenomenon can increase

Pb contents also in the aquifers and seriously compromise the health of the environment and of the whole ecosystem, even on a large scale. In Western Countries the major peaks of Pb concentrations in air have been registered during the 70's and the 80's, when lead alkyls were widely diffused as antiknock agent in petrol (Flament et al., 1996; Von Storch et al., 2002). Due to the well-known Pb toxicity, the use of these alkyls in the gasoline production, has been gradually banned by some Country Authorities, even if, in most of the developing countries it's still widely used. The introduction of unleaded gasoline in Europe and in countries such as Canada, USA and Japan, has slowly changed the isotopic composition of atmospheric aerosols, and the industrial processes have become the main sources of Pb contamination (Rosman et al., 1994; Veron et al., 1999a,b).

The reason why Pb isotopes are so commonly used as tracers of anthropogenic pollution, is their very high isotopic stability even after very long periods. The isotopic fingerprint of a Pb source is the result of the age of the ore body itself and its initial U, Th and Pb contents (Doe, 1970). This means that, the isotopic ratios measured, for example, on an industrial waste, reflect the same isotopic ratios of the source in which has been extracted the Pb used for that specific industrial process. Lead isotopes, can, therefore, be considered to be a reliable source tracer, but also an useful tool to follow the migration and the distribution patterns of the elements through the different media. In Campania Region Pb isotopic studies for environmental purposes have started in recent years: in 2002, Pb isotopes have been used to characterize an industrial site under remediation in the Neapolitan area (Bagnoli) (Tarzia et al., 2002), in 2008 Cicchella carried out a research on the Pb contents in the urban soils of Naples (Cicchella et al., 2008) and in 2009-10 isotopic studies on soils and groundwaters of the Domitio-Flegreo Littoral an Agro Aversano have been realized by Grezzi (Grezzi et al., 2010) and Bove (Bove et. al., 2010). In these three works the obtained results strongly suggest a mixing between two main end-members: one of natural origin (geogenic) (Ayuso et al., 1998; Gilg et al., 2001; Somma et al., 2001; D'Antonio et al., 1995) and one deriving from anthropic sources.

2 Studied area

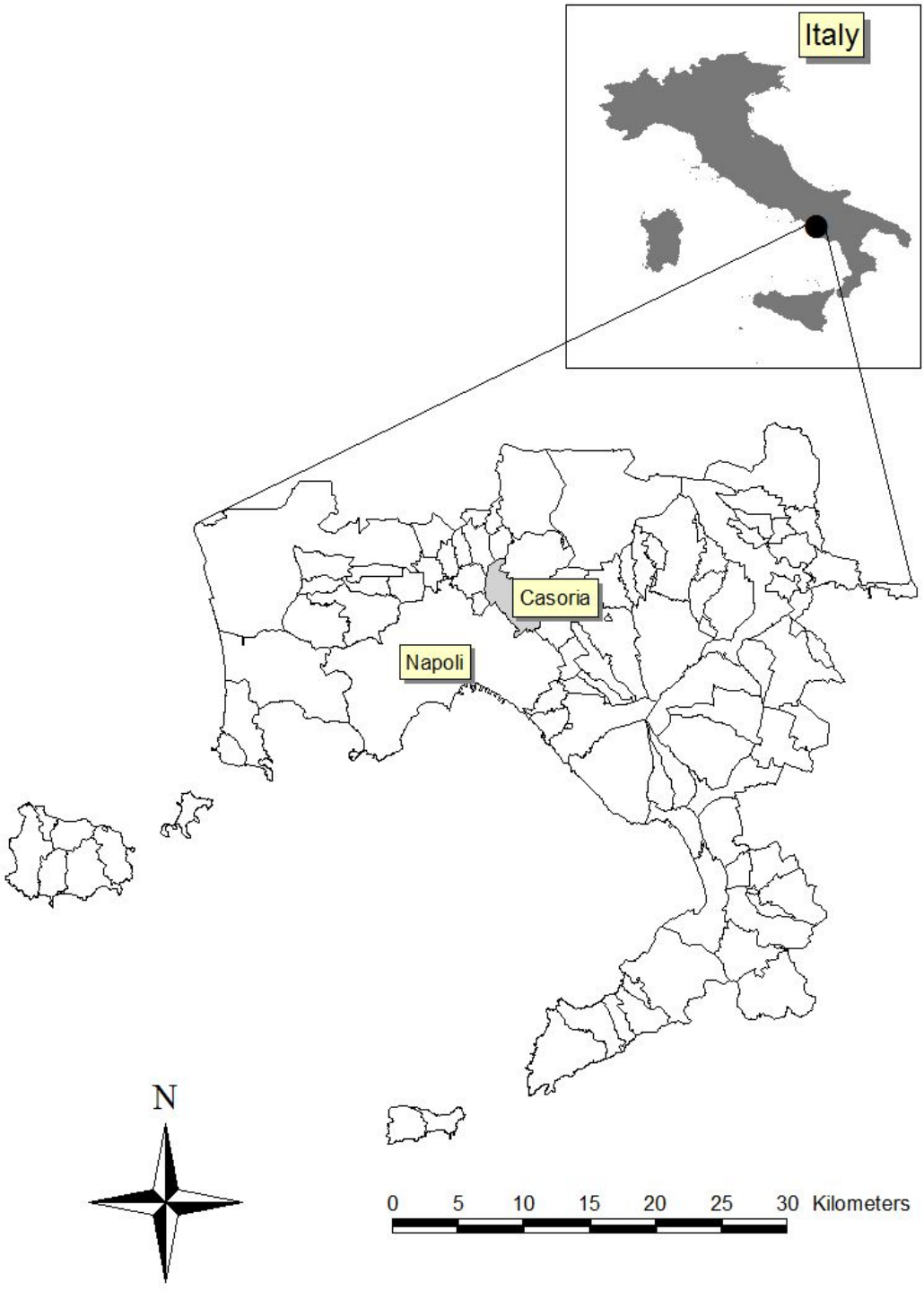


Figure 1 Province of Naples map and Comune di Casoria studied area

Casoria is located on the north-east side of Naples and extends for about 12 Km^2; it is included in the Campanian Plain which contains the Neapolitan area and part of Caserta province (Fig 2).

Figure 2 Comune di Casoria studied area

In this area the processes of urbanization and industrialization have certainly been a powerful factor for social and economic development, principally in the last 100 years, but also have altered the delicate balance of nature, which was at the beginning of the XX century the principal economic resource, made by agriculture and farming (vineyards, fruit trees and hamp).

Since the late 20 years, industrial development, that made Casoria one of the most important industrial settlements of the Neapolitan area (Montefibre chemical Company, the principal one) is slowly stopped and actually is still present Alenia aeronautic work Company, related to the International Airport of Naples (Capodichino) that is located on the board between Napoli and Casoria.

2.2 Geology: The Campanian Plain

Casoria is located in the middle part of the Campanian Plain (Fig. 3), a big graben, probably originated in the Lower Pleistocene, which, during all the Quaternary, developed with a subsidence velocity of about 1.5-2 mm/year. Alluvial deposits deriving from the Apennine erosion, and volcanites deriving from both ancient volcanic complexes, now buried, (Parete volcano and Pre-Somma volcano) (De Vivo et al., 2001; Rolandi et al., 2003) and from the modern complexes of the Campi Flegrei and Somma-Vesuvio, have gradually filled the subsident graben. The Campanian Plain is delimited by NE-SW and NW-SE normal faults that lowered part of the Apennine Carbonatic Platform which now represents the substratum of the whole Plain (De Vivo et al., 2006a).

According to Scandone (1979), the Campanian Plain was generated by the same tectonic processes that caused the opening of the Tyrrhenian Sea and the counterclockwise rotation of the Italian peninsula.

Casoria is principally a plan (between 10 to 70 m on sea level), made by Neapolitan Yellow Tuff (depth 10-20 meters) highly consolidated with pozzolana and lapilli layers covered by piroclastic sediments.

The southern sector is morphologically the low level of the plan, and was a swampy territory until XIX century when it was reclaimed.

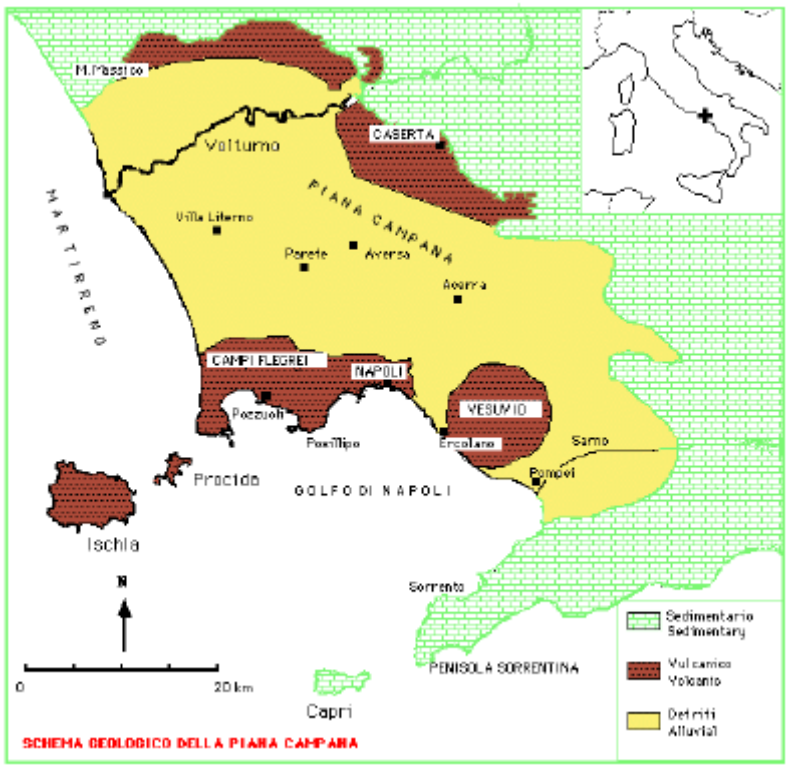


Figure 3 Campanian plan geological settings

2.3 Land use

To get an idea of potential source of contamination, detect land use is often first research to do in an environmental study.

Comune di Casoria is for 60% very high urbanized area, it is possible to detect a northern sector in which is present the original historical settlement, and Frazione Arpino in the southern sector.

Industrial and commercial areas (30%) are located in the south-centre of Casoria, along or closed important routes (via nazionale delle puglie and asse mediano).

Rural activities or farming are located in northern and southern sector but are extremely little and just for family supply (Fig. 4).

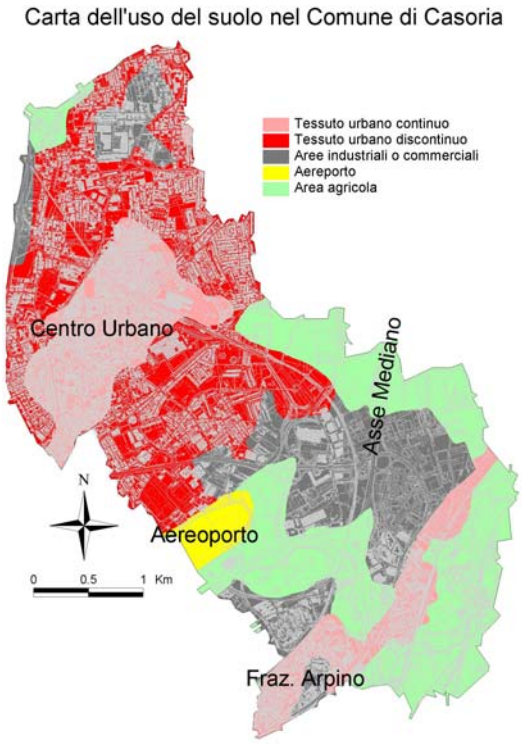


Figure 4 Comune di Casoria land use map (Corinne project)

From the 60' to 90's Casoria was one of the principal industrial areas in the south of Italy, in which important industrial settlements were built:

- Montefibre-Rhodiatoce (Petrochemical works)
- Resia (Chemical resins production)
- ADS-Acciaierie del Sud (Steel works)
- Calcobit (Concretes works).

Industrial developing has been the reason of the high urbanization of this area starting at the beginning of 60' which consists in 30,000 habitants' increment in 30 years.

In the 90' new economic trends resulted in the closure of all the principal industrial settlements of Neapolitan area, so Casoria economy and works get stopped.

Results of 30 years of industrialization are brownfield areas where the principal industries were built, and potentially high level of contamination in all the municipal area with consequences on public health.

3 Sampling

3.1 Introduction

In order to have a good and spatially well extended knowledge about the major elements concentration in the Casoria municipal area, different kind of environmental media have been sampled: surface soils, soil profiles and tap waters.

All the sampling procedures have been done on the basis of a square grid overlapped to the whole studied area; every cell has been uniquely identified by an alphanumerical code (i.e. CAS001).

Every sampling phase and every sampling site has been documented by pictures and notes taken during field activities; all these data have been put together into an appropriate database in order to make easier the localization of each site for further investigations or comparisons.

3.2 Soils and water sampling

The field activity has been developed in three main and well distinct phases:

- The first sampling, made in May 2008, consisted to collect 8 topsoil samples (depth 5-20 cm) distributed on all the municipal area, to detect PCB's, Dioxins and Furans values to get information on potential contamination due to anthropic activity related to industrial activities or waste disposal and burning.
- Between June to August 2008, second sampling phase was carried out. It consisted to collect 126 topsoil samples (depth 5-15 cm). The whole field activity was realized on the basis of a sampling grid made up cells of 300 m X 300 m extension each; FOREGS sampling procedures (Plant et al., 1996; Salminen et al., 1998) have been strictly followed during all the steps.
- Last sampling has been completed in July 2009 in order to collect 50 samples from 5 soil profiles (0-100 cm, 1 sample each 10 cm) in areas which showed Pb higher level of concentration.

5 tap water samples, collected in February 2010, were send to USGS Radiogenic Isotope Laboratories (Reston, VA) for Pb isotope studies.

4 Methodologies

4.1 Sample preparation and chemical analysis

Surface soils

After being dried with infra-red lamps at a temperature constantly kept below 35°C, the 126 surface soils, have been pulverized in a ceramic mortar and then sieved at the < 100 mesh fraction (150 mm). The obtained pulps have been stored in small plastic bags containing at least 30 g of samples, and then shipped to the ACME Analytical Laboratories Ltd (Vancouver, Canada), accredited under ISO 9002. They have been analyzed by ICP-MS technique after aqua regia digestion (Cicchella et al. 2008), for the determination of the following 53 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge,

Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr. The aqua regia attack is considered to be one of the best total dissolution processes: it dissolves metals in water soluble salts, in cation-exchange sites, in clay particles, in organic chelates, in amorphous Mn and Fe oxides and hydroxides, in carbonates, in sulphides and in some sulphates. Aqua regia also partially solubilizes metals in ferromagnesian-rich silicates and some Fe, Ti and Cr oxides. The most resistant minerals to this kind of attack are the Ta, Hf, Zr, Nb and Ba sulphates.

In the Lab about 15 g-split of each powdered soil sample were digested in 45 ml of aqua regia (2:2:2 of HCl:HNO3:H2O) at 95° C for about one hour; the obtained solution was then taken to a final volume of 300 ml with 5% HCl. Aliquots of sample solution were aspirated into a Perkin Elmer Elan 6000 ICP-mass spectrometer.

In Table 1 the instrumental detection limits (DL) for each element are reported.

Analyte	MDL	Analyte	MDL
Mo ppm	0.01	Al %	0.01
Cu ppm	0.01	Na %	0.001
Pb ppm	0.01	K %	0.01
Zn ppm	0.1	W ppm	0.1
Ag ppb	2	Sc ppm	0.1
Ni ppm	0.1	Tl ppm	0.02
Co ppm	0.1	S ppm	0.02
Mn ppm	1	Hg ppm	5
Fe %	0.01	Se ppm	0.1

As ppm	0.1	Te ppm	0.02
U ppm	0.1	Ga ppm	0.1
Au ppb	0.2	Cs ppm	0.02
Th ppm	0.1	Ge ppm	0.1
Sr ppm	0.5	Hf ppm	0.02
Cd ppm	0.01	Nb ppm	0.02
Sb ppm	0.02	Rb ppm	0.1
Bi ppm	0.02	Sn ppm	0.1
V ppm	2	Ta ppm	0.05
Ca %	0.01	Zr ppm	0.1
P %	0.001	Y ppm	0.01
La ppm	0.5	Ce ppm	0.1
Cr ppm	0.5	In ppm	0.02
Mg %	0.01	Be ppm	0.1
Ba ppm	0.5	Li ppm	0.1
Ti ppm	0.001	Pd ppb	10
B ppm	20	Pt ppb	2

Table 1 Instrumental Detection Limit values

Only few samples have concentrations below detection limit for some analysed elements. A conventional substitution of the non registered value with an assigned value corresponding to 50% of the detection limit, has been applied.

Actually profile soil samples chemical data are not yet available, and will be inserted in the "Geochemical Atlas of Comune di Casoria"(Civitillo et al. in press), but the high intensity of surface sampling procedure, should be enough to get an idea of Pb contamination level in the Casoria metropolitan area, and useful to get a good correlation with the isotopic data that has been carried out..

4.4.1 Quality controls

In order to process only those data that have a good analytical value, quality controls on the laboratories data have been applied.

Tables 3 and 4 list the accuracy and precision values of the Casoria sample's geochemical data considered in this work, after the application of the chosen analytical technique.

Accuracy

Accuracy is defined as the degree of closeness of the measurement of a quantity to its true value. The laboratory accuracy error has been determined using the formula:

$$A(\%) = \left(\frac{|X - TV|}{TV}\right) * 100$$

with: X= laboratory's analysis result for the standard sample,
TV= true value of the standard sample.

For the measurement of the analysis accuracy error, Acme's in-house reference materials have been used: for soil samples the standard was DS7.
Acceptable accuracy error values don't have to be over 15%.

Precision

Precision is defined as the degree of reproducibility of a measurement; in other words is the degree of how, repeated measurements, show the same results under the same conditions.

The precision has been calculated as relative percentage difference (%RPD) using the formula:

$$\%RPD = \left[\frac{|SV - DV|}{((SV + DV)/2)}\right] * 100$$

with: SV= original sample value,
DV= duplicate sample value.

Precision of the performed analysis, has been calculated on 6 in-house replicates and one blind duplicate for soils
Values can be considered good if the RPD is < 35% for soils; no one of the 15 elements considered exceed the limit of 35%

4.2 Sample preparation for Pb isotopes analysis

Surface soils and soil profiles

The 50 soil profiles, after the collection, have been prepared and analyzed at the USGS Laboratories in Reston (VA, USA). Here the samples have been air-dried and sieved at < 60 mesh fraction (250 mm). In order to determine whether the content of metals in soils is mainly due to anthropic or geogenic contribution, a leaching procedure has been applied to them. The acid 25 mixture used for this is a 1.5N HCl+3N HNO3 solution, which preferentially dissolves amorphous Fe- and Mn-oxyhydroxides, whose coatings are considered to catch most of the anthropogenic Pb. About 200 mg of each sample have been leached with 3 ml of the acid solution, placed in an ultrasonic bath and centrifuged for 5 minutes. The product of this operation are two fractions of the same sample inside the tube: one liquid (leached, L), and one at the bottom of the tube in a solid state (residue, R). The residue samples have been directly placed on warm hot plates to dry at < 50°C while, the leached portion of the soils have been first digested in an Ethos Plus Microwave Lab Station for 15 minutes and then put to dry (Fig. 5).

Figure 5 Soil samples digestion on Ethos Plus Microwave Lab Station

Once dry, the samples have been processed and evaporated using a multistep chemistry procedure with different amount of concentrated HNO3, concentrated HF, 4N HCl and 0.5N HBr. In order to separate Pb, samples were finally passed through Pb exchange columns by using an anion-exchange resin, 0.5N HNO3 and 0.5N HBr (Ayuso et al., 2004).

In order to ensure the maximum purity of the extracted Pb, the step of the exchange columns has been made twice. The entire procedure has been applied to the 20 duplicate samples of surface soils too.

4.3 Geochemical data elaboration

Geochemical data elaboration has been performed on all 52 analysed elements and has been reported in the Geochemical atlas of Comune di Casoria (Civitillo et al., in press). Here only selected elements most significative for environmental purpose will be discussed..Particularly 15 elements which are reported and considered potentially dangerous by Italian environmental law D.Lgs.152/06.

4.3.1 Univariate statistics

A traditional statistical analysis of the soils analytical data (Sinclair, 1976), has been performed by KaleidaGraph 4.0 program.

The distribution of the elemental concentrations for all the 126 soil samples has been plotted using histograms and cumulative frequency curves .

Due to the small number of water samples collected, it wasn't possible to make an appropriate statistic elaboration for them too.

4.3.2 Geochemical map production

In this part of the work are presented and described the various types of geochemical maps compiled for the chemical elements in soil analyzed by the Comune di Casoria area.

Dot map: is the map of dot distribution of concentrations, useful for information on the actual concentration distributions when the sample was collected.

Interpolated map: interpolated data maps provide to get information of a kind spatial range. In fact, it is not possible to know the actual concentration at any point the study area, this type of map is the best possible approximation of the actual concentration values at points not sampled

Based on the cell size used during the sampling is possible, using a detected radius interpolation related to the element concentration, to reclassify the dot value on a spatial value through a Multifractal Inverse Distance Weighted (MIDW) method (Cheng, 1999) available in the software GeoDAS (Cheng, 2003); To produce interpolated maps the multifractal analysis filter method used is Concentration-Area model (C-A).

Baseline map: In this work has been also produced baseline maps. This kind of maps are the principal way to get information about the statistically higher concentration levels found in a detected area

On literature **t**he term background content (natural background) is meant the concentration of natural elements, including the presence of abnormal concentrations due to mineralization. The term baseline should mean measured concentrations of elements present in a given site, including, therefore, the presence of elements of anthropogenic origin. In the case of Casoria soils, which reflect the presence of a strong anthropogenic contribution, is important specify that the maps produced are "baseline levels" and not "background levels".

To produce this kind of maps the same procedure conduced for Interpolated maps were used, the difference is the multifractal analysis filter method: S-A (Spector & Grant).

So data obtained from the ICP-MS analysis on surface soils, statistically and geochemically studied by multifractal methods have been processed through the ArcView GIS 3.2 software for map elaboration. According to the detection limits for each element, Dot, Interpolated and Baseline maps were produced.

4.4 Pb isotopes analysis

4.4.1 Pb isotopes

Lead has four stable isotopes: 208Pb, 207Pb, 206Pb and 204Pb; three of them (208Pb, 207Pb, 206Pb) derive from radioactive decay of 232Th (208Pb), 235U (207Pb) and 238U (206Pb), while the 204Pb isotope is the only one non radiogenic. Each natural material has its own characteristic Pb isotope ratio which is the result of the different half-lives of Th and U and the primordial U/Th/Pb availability in that material. During geologic eras the combination of these key factors has lead to the production of an isotopic signature for each Earth's reservoir (Faure, 1986; Dickin, 1995; Galer and Goldstein, 1996). Furthermore, environmental and industrial processes do not fractionate Pb isotopes, and the different

materials keep their original source ratios. This isotopic stability makes the Pb isotopes an useful tool to trace contamination sources, both for geologic (natural Pb contents in bedrocks) and anthropic sources (isotopic signature of the ore body in which, Pb for human activities, has been extracted) (Ayuso et al.,2008; Kramers and Tolstikhin, 1997).

4.4.2 Thermo Ionic Mass Spectrometer (TIMS)

Lead isotopic analysis on 8 surface soils, 5 soil profiles and 5 tap waters have been run in the Radiogenic Isotope Laboratory of the US Geological Survey in Reston, VA. For these analysis a Finnigan-MAT 262 Thermal Ionization Mass Spectrometer (TIMS) with a Faraday multi-collector cup, was used (Fig.6).

Figure 6 Finnigan-MAT 262 Thermal Ionization Mass Spectrometer (TIMS)

The Pb collected through all the chemistry and elution procedures for each soil sample, has been loaded on a single post Re degassed filament by using the method of silica gel and phosphoric acid. The phosphoric acid's main properties for this application are: displacing all other anion species, destroying organic residues and gluing the sample to the filament. Silica gel acts as a blanket over the sample and retards Pb volatilization (Cameron et al., 1969) thus permitting the heating of the filament until the wanted temperature, without losing the Pb.

Filaments have then been loaded on a 13 samples carousel and put into the turret position of the TIMS. Once in the machine, under high vacuum condition, high voltage has passed through the filament which slowly and gradually heated until an evaporation value of 1800 mA. Through heating, the sample, has been atomized and ionized and a stable ion beam formed. The beam, accelerated by the electrical potential gradient, was focused by a series of slits and electrostatically charged plates and directed through a big magnet. The magnetic field separated the initial ion beam into different beams on the basis of their mass to charge ratio; these beams finally reached the collectors where, were converted into voltage and, through the comparison of voltages, lead isotopic ratios were measured.

Isotopic mass fractionation has been constantly monitored by periodic analysis of a standard (NIST-SRM981). The obtained isotopic ratios were corrected for mass fractionation relative to this standard.

5 Results and discussion

5.1 Statistical data

The main statistical parameters (minimum value, maximum value, mean, median and standard deviation) of the data obtained from the ICP-MS analysis, are reported respectively in Table 2.

Statistical Data					
Element	Max	Min	Media	Median	Standard Deviation
Mo ppm	5.7	0.77	1.52627	1.36	0.685325889
Cu ppm	1034.3	11.42	108.8137	95.565	101.9258245
Pb ppm	821.42	25.28	125.7006	103.135	104.6515535
Zn ppm	1765.1	42.5	199.7484	141.1	211.222651
Ag ppb	3844	32	378.5794	262	463.4414975
Ni ppm	70.2	3	14.46349	14.45	6.841024522
Co ppm	25	3.2	8.98254	9	2.522001725
Mn ppm	978	332	658.119	663	113.8213061
Fe %	3.12	1.26	2.190635	2.18	0.349286693
As ppm	33.9	5.8	14.06349	13.7	3.395964739
U ppm	6.4	1.8	3.506349	3.4	0.908074537
Au ppb	333.5	0.5	25.78413	16.2	38.08717666
Th ppm	22.8	1.8	11.67698	12.1	3.701635589
Sr ppm	284.7	100.3	175.5349	175.5	33.98104017
Cd ppm	3.5	0.1	0.520635	0.425	0.444672906
Sb ppm	11.15	0.02	1.44405	1.16	1.432213077
Bi ppm	1.53	0.21	0.50373	0.48	0.174198664
V ppm	85	30	57.07143	56.5	11.91112325
Ca	14.25	0.77	3.126984	2.15	2.536644483
P	1.662	0.036	0.191214	0.171	0.151934176
La ppm	52.4	17.5	39.16746	39.55	7.040248057
Cr ppm	486.1	2.2	20.68968	15.5	43.1037443
Mg	1.1	0.22	0.579365	0.605	0.140779237
Ba ppm	2630.6	191	404.896	367.95	270.3771293
Ti ppm	0.17	0.048	0.107587	0.107	0.022025538
Al	5.61	1.98	4.115317	4.11	0.708935751
Na	1.128	0.197	0.473508	0.4505	0.162016332
K	2.37	0.65	1.351111	1.325	0.363140132
W ppm	1.9	0.4	1.134921	1.1	0.190711283
Sc ppm	2.5	0.8	1.696825	1.7	0.347318069
Tl ppm	0.17	0.6	1.628492	1.63	0.383487298
Hg ppm	986	11	227.8651	178.5	171.2851355
Se ppm	1.3	0.2	0.450794	0.4	0.162847674
Te ppm	0.1	0.02	0.042241	0.04	0.014085837
Ga ppm	10.9	3.5	8.128571	8.35	1.519729299
Cs ppm	21.45	5.57	13.89421	14.035	3.311630983
Hf ppm	0.47	0.09	0.246825	0.24	0.071135373
Nb ppm	13.35	0.87	6.327381	6.315	2.663382565
Rb ppm	211.1	71.5	141.4849	142.4	34.39060352
Sn ppm	35.4	1.9	6.629365	5.6	4.198019866
Zr ppm	46.2	6.3	23.45159	23.3	7.845352603
Y ppm	17.14	5.42	11.1473	11.21	1.983295203
Ce ppm	102.9	31.1	74.33889	75.8	14.11393055
Be ppm	8.4	1.8	5.121429	5.1	1.299637312
Li ppm	38.8	9.6	21.21587	21.45	4.723463351

Table 2 Statistical data elaboration values

Data related to surface soils have been statistically and cartographically elaborated to realize a complete suite of dot, interpolated and baseline geochemical maps. In order to compare obtained data, to recognize if positive or negative trend exist between Pb and all the other elements the concentrations of each element have been plotted versus Pb. On X axis Pb extreme values (up to 800 mg/kg) has been removed to show the related trend between different elements which considering all the data should be difficult to be understood. Maximum Pb values considered are 140 mg/kg for all data and 40 mg/kg for industrial area samples. Here only Zn and As versus Pb has been reported (Figs. 7- 8)

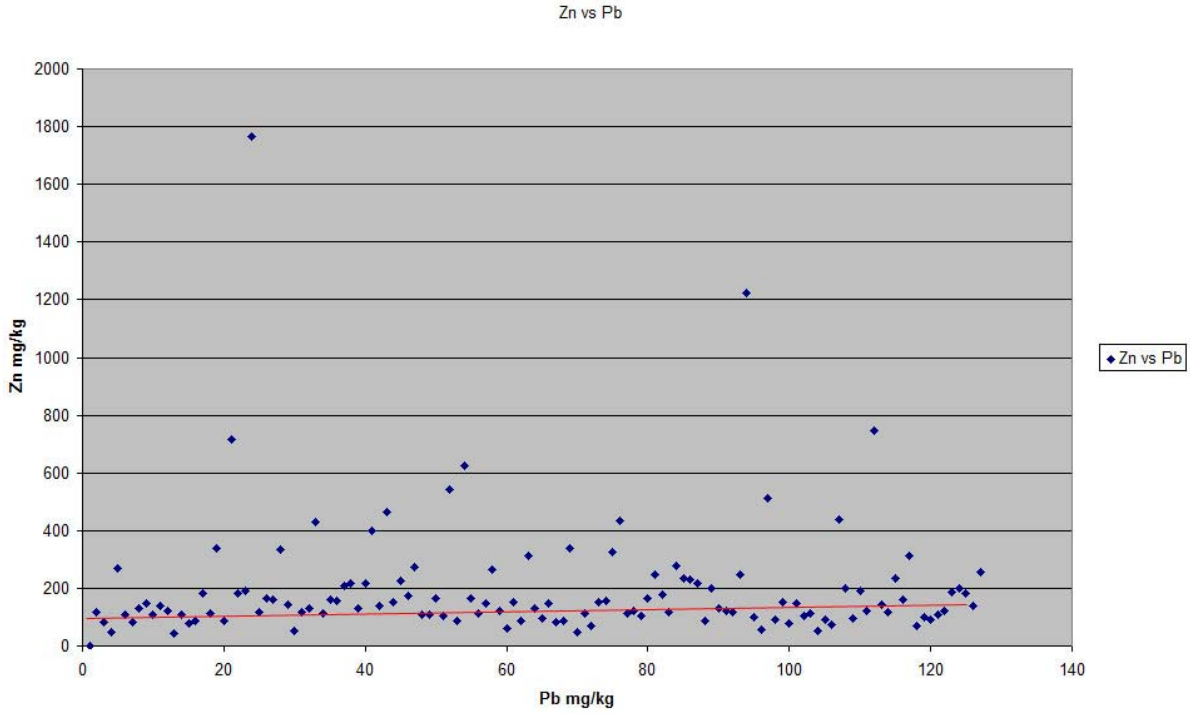


Figure 7 Pb vs Zn Plot

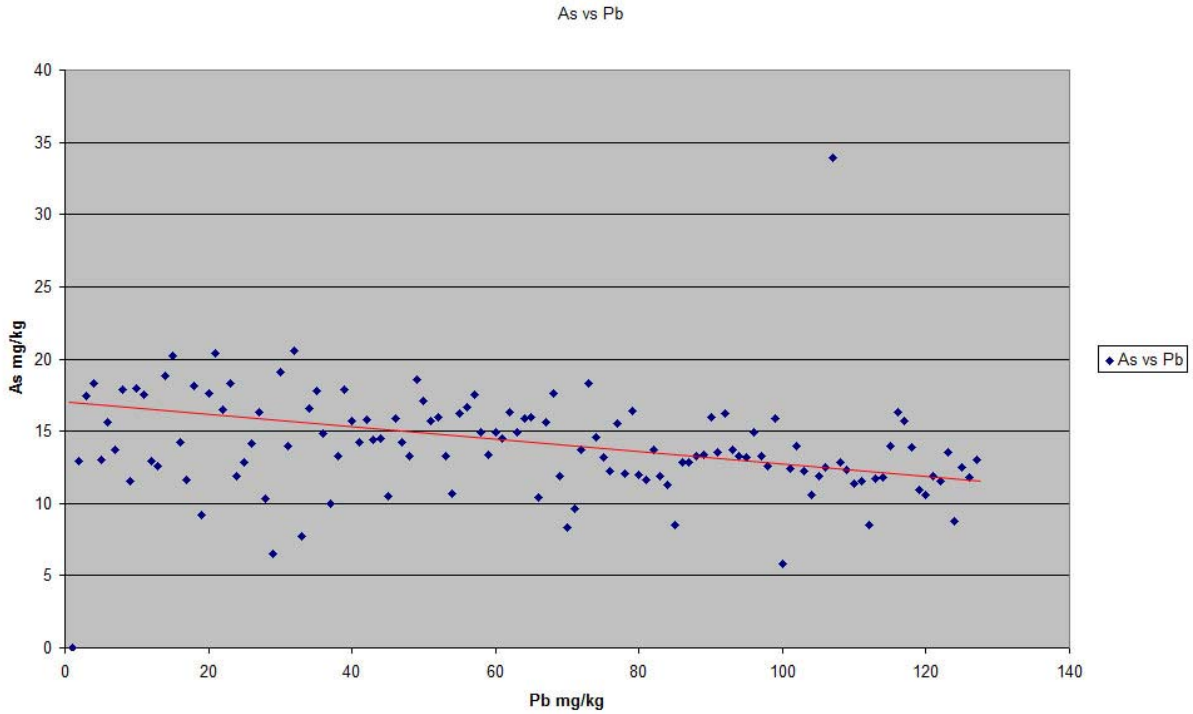


Figure 8 As vs Pb Plot

Data obtained and compared shows two different trend:

- Principal elements related to anthropic and industrial activities as Zn, Cd. Hg, etc.. show positive or normal trend against Pb.
- As shows negative trend against Pb, probably due to the different source of contamination.

To identify if the potential contamination by Pb, Zn, Cd, is strictly related to industrial activities, and if As concentration is characteristic by geogenic source and not related to anthropic activities, the same plot has been produced considering only the samples closed to the industrial or ex industrial settlements (Figs. 9-10).

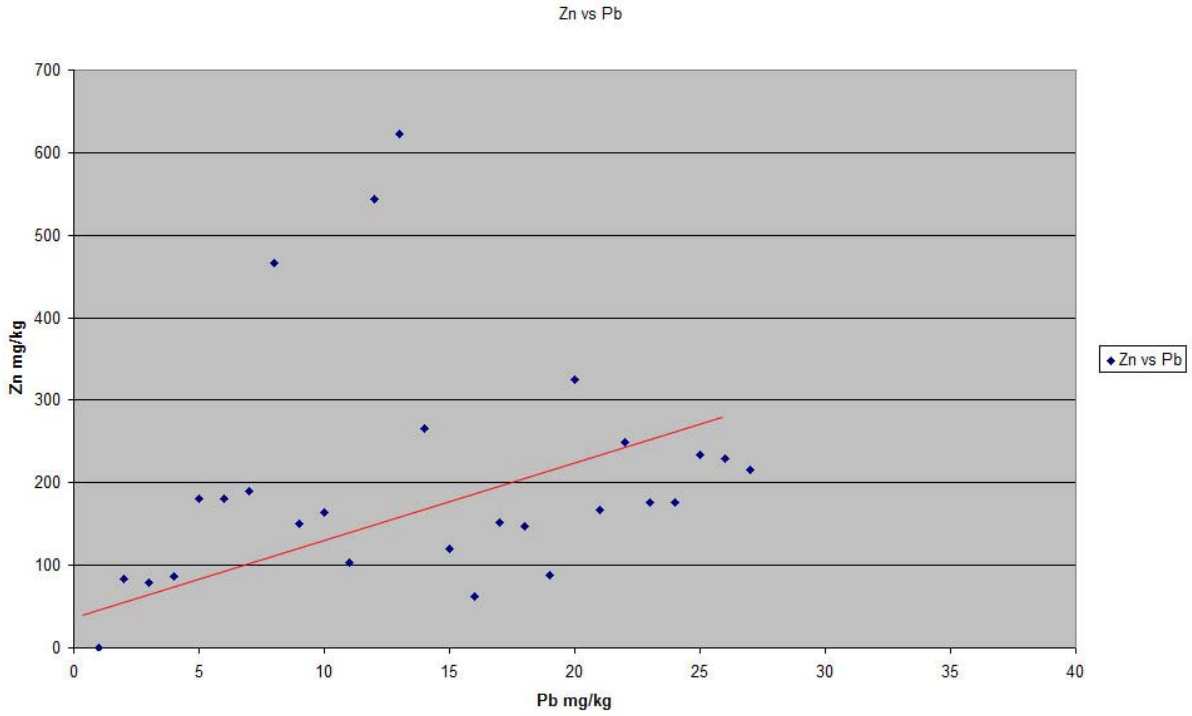


Figure 9 Zn vs Pb Plot (industrial areas)

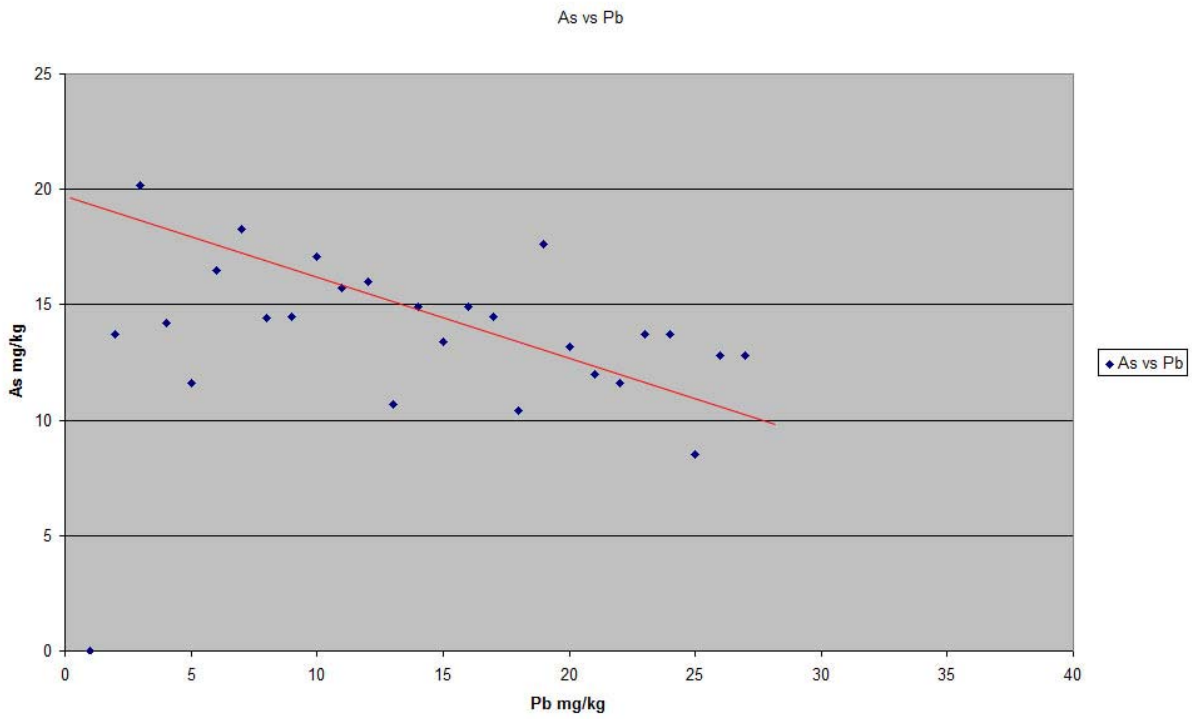


Figure 10 As vs Pb Plot (industrial areas)

Observing data plot using samples taken closed to industrial areas, positive and negative trends becomes extremely clear, confirming what appear on previously plots.

- Zn group shows positive trend against Pb confirming that the anthropic origin is characteristic of these elements.
- As shows negative trend against Pb confirming that anthropic components is not present, and that geogenic imprinting is characteristic for the As concentration.

5.2 Geochemical - environmental cartography

In recent years the geochemical cartography has been widely used as a powerful tool in different geology branches, from the geochemical exploration to the environmental geochemistry. A geochemical map can be seen as a picture of the health of an investigated area and helps in outlining the main geochemical trends, even at a large scale (De Vivo et al. 2009).

In 1994 the IUGS/IAGC Global Geochemical Baselines Programme established the need of a global geochemical reference baseline for more than 60 elements in different environmental media. In Europe this directive has been carried out by the Forum of European Geological Surveys (FOREGS) which, in 2005 realized the Geochemical Atlas of Europe (Darnley et al., 1995; Salminen et al., 1998, 2005, 2006) by using, in each participating country, standardized sampling methods, analysis and data elaboration (Salminen et al., 1998).

In Italy the first geochemical maps produced, were realized for mining purposes in Calabria, Sardinia, Southern Tuscany and on Peloritani Mountains (De Vivo et al., 1998a, b, c; 2001) by scientists from University of Naples "Federico II", University of Siena and University of Cagliari.

Autonomous researchers groups realized different scale geological atlases in order to achieve the goal of a complete national geochemical database. Thus, since 2006, a large number of atlases realized on the basis of the FOREGS directives, have been produced: the atlas of the Campania region (De Vivo et al., 2006a), the atlases of Avellino, Salerno, Caserta and Benevento urban areas (Albanese et al., 2007; Cicchella et al., in press; Lima et al.,2007; De Vivo et al., 2006-a; Fedele et al.,2008), and the atlas of Ischia island (Frattini et al., 2006). Furthermore, implementing in southern Italy the sampling accomplished for the Geochemical atlas of Europe, a Geochemical atlas of Italy was produced too (De Vivo et al., 2009).

The geochemical maps realized following these procedures, are a clear and useful tool for local authorities and environmental protection agencies, who need to address the public concerns regarding the toxic element pollution threat to ecosystem and human health.

Moreover the atlases are a sound basis for policy makers and help them to face environmental pollution and related legislation with more consciousness.

The maps shown here are those related to the concentrations of the major potential harmful elements and of all those elements whose concentration limits have been fixed by the 152/06 Italian Environmental Law (Tab.3).

Elements	Intervention threshold residential use	Intervention threshold industrial use
As (mg/kg)	20	50
Be (mg/kg)	2	10
Cd (mg/kg)	2	15
Co (mg/kg)	20	250
Cr tot (mg/kg)	150	800
Cu (mg/kg)	120	600
Hg (mg/kg)	1	5

Ni (mg/kg)	120	500
Pb (mg/kg)	100	1000
Se (mg/kg)	3	15
Sb (mg/kg)	10	30
Sn (mg/kg)	1	350
Tl (mg/kg)	1	10
V (mg/kg)	90	250
Zn (mg/kg)	150	1500

Table 3 D.Lgs. 152/06 residential and industrial limits

For each of 15 selected elements there is a brief description of its chemical properties and of its influence on human health (<http://www.lenntech.com/periodic/periodic-chart.htm>); then the related dot, interpolated, baseline and risk maps, are shown with its basic statistics graphs (histograms, cumulative frequency curves, and box plot).

Figure 11 Soil sampling sites

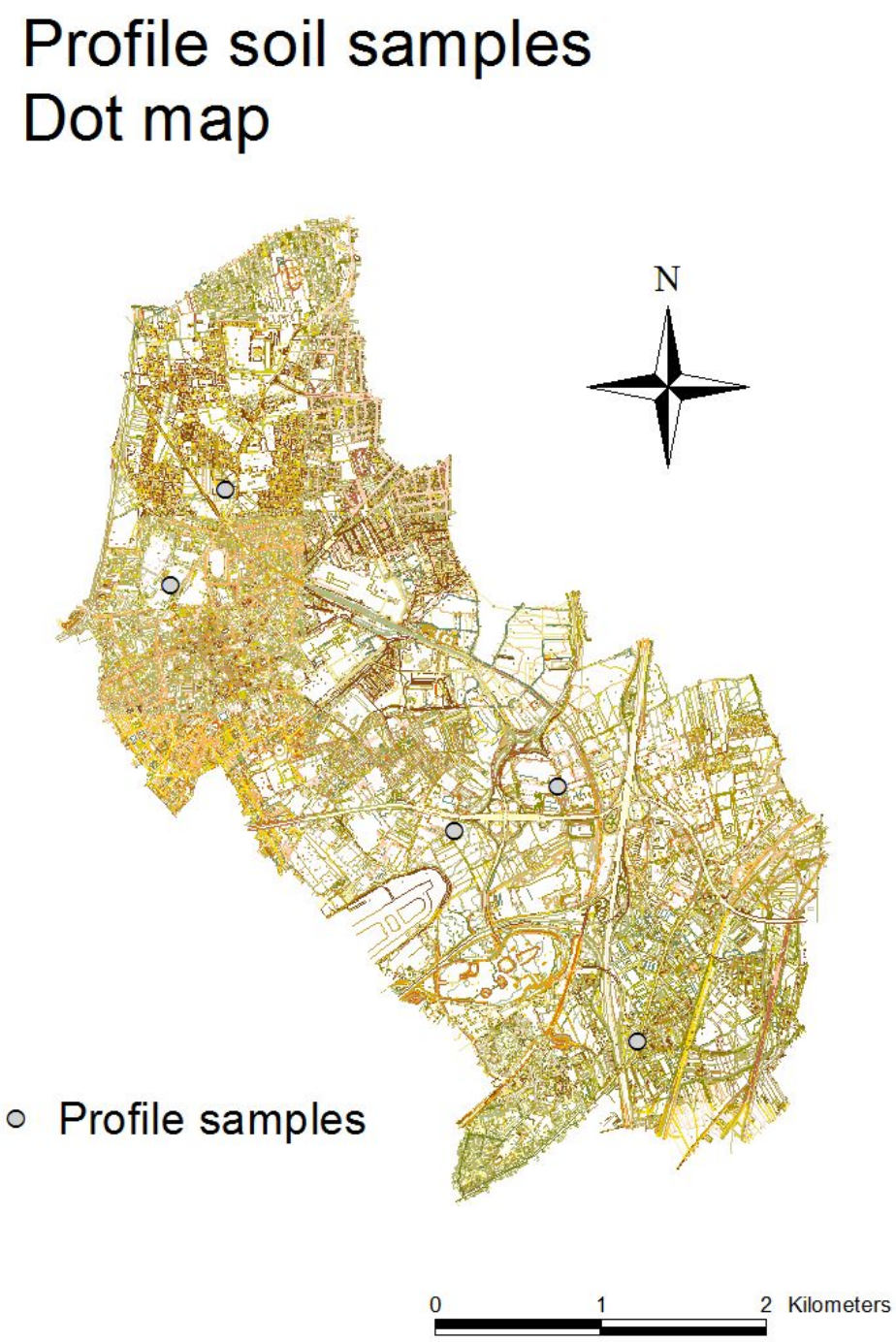


Figure 12 Profile sampling sites

Arsenic (As)

Arsenic is a metalloid belonging to the VA group of the periodic table of the elements; it is, at same time, one of the most toxic elements for human beings, but also an ultra-trace micronutrient for both humans and animals.

Arsenic compounds are mainly used as a wood preservative and for the production of special types of glass. In past years arsenic compounds have been widely used for agricultural activities as pesticides, but now are banned in a large number of countries. It naturally occurs in soils and minerals, especially with sulphur in minerals such as arsenopyrite (AsFeS), realgar, orpiment and enargite. Natural arsenic in the atmosphere comes from volcanoes (about 3000 ton/year) and microorganisms (about 20.000 ton/year), but anthropic arsenic deriving from burning of fossil fuels, is responsible for the highest emission of As in the atmosphere: about 80.000 ton/year. Arsenic is mainly emitted in the environment by the copper producing industries, but also during lead and zinc production and in agriculture.

Arsenic is an element with a very low water-solubility and that hardly converts to volatile products. Due to human activities, especially mining and melting, naturally immobile arsenics have mobilized and widespread.

Humans may be exposed to arsenic through food, water and air. but also through skin contact with soil or water that contains high arsenic levels. Inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. Probably the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development. Inorganic arsenic can also damage DNA. Organic arsenic can cause neither cancer, nor DNA damages, but exposure to high doses may cause certain effects to human health, such as nerve injury and stomachaches. A lethal dose of arsenic oxide is generally about 100 mg.

Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

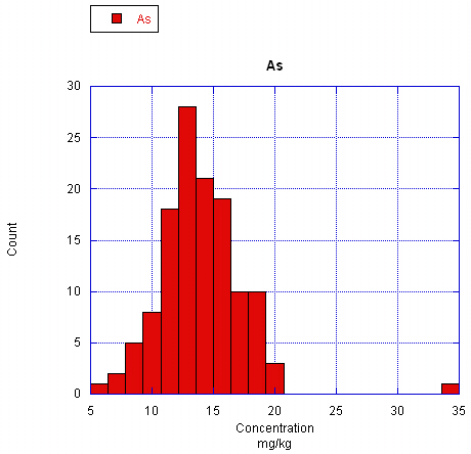
It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on many locations on earth and for long periods.

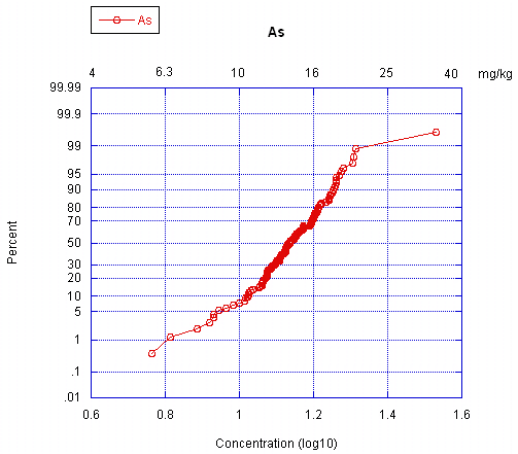
Distribution of As concentrationts

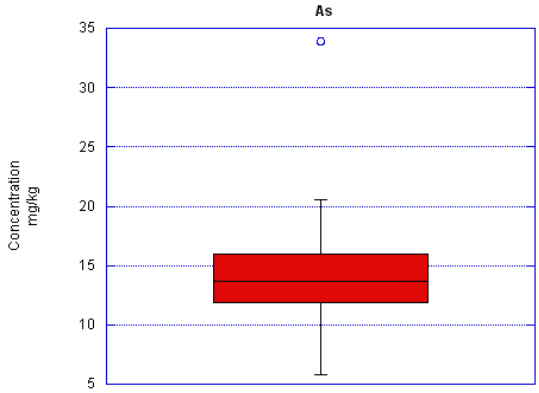
Soils of the entire Neapolitan territory are characterized by quite elevated As baseline values up to a maximum of 60 mg/kg (Cicchella et al. 2005). These baseline values coincide with natural background values because of the diffuse presence of hydrothermal fluids related to geothermal activities in the Neapolitan volcanic fields (Tarzia *et al*. 2002; Lima *et al*. 2003b).

The high As concentrations in the Casoria soils (20-34 mg/kg) detected in the northern area, are clearly consistent with the enrichment values in the local volcanic rocks.

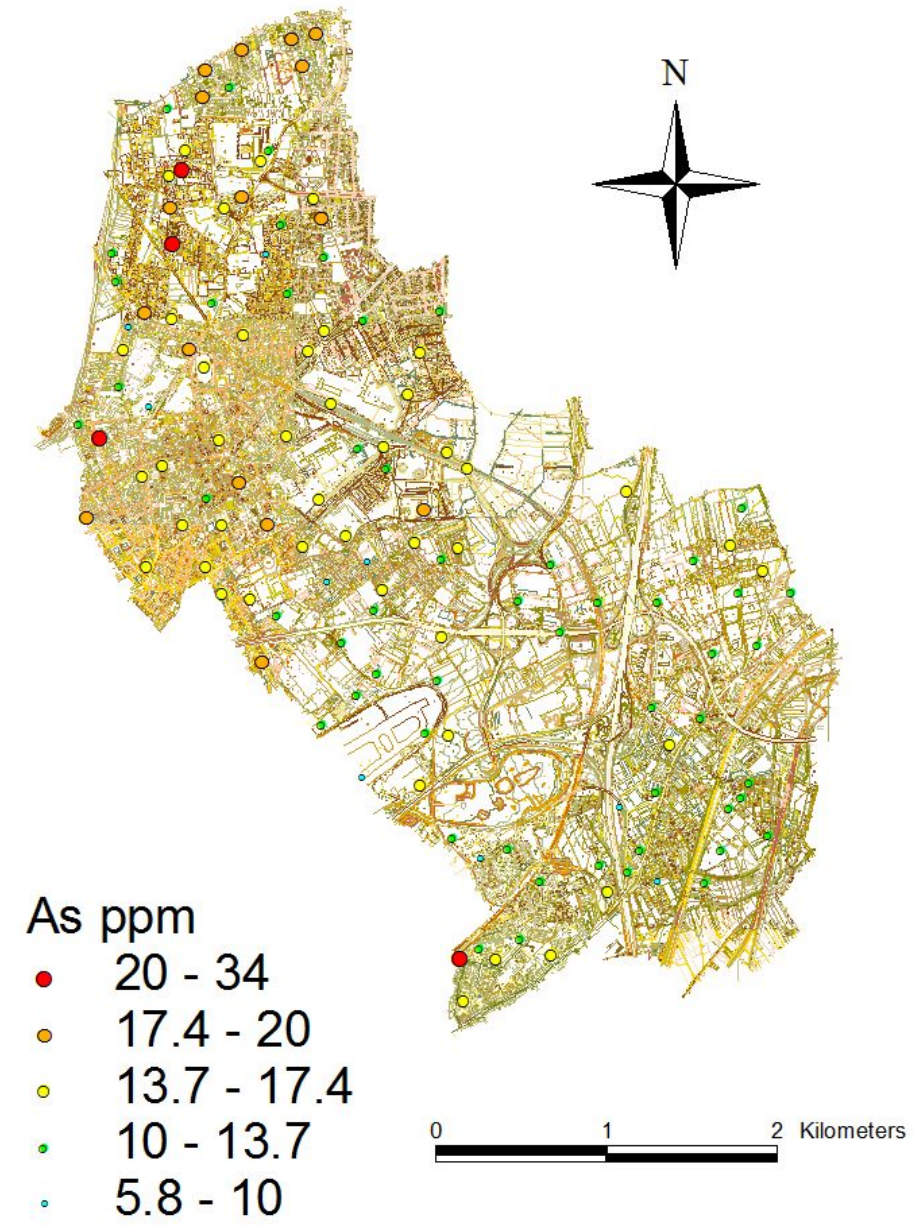
Environmental Italian law fix As concentration limit for residential areas (20 mg/kg) and for industrial areas (50 mg/kg). Casoria As values are mostly below residential area threshold, just 4 samples showes higher concentrations.

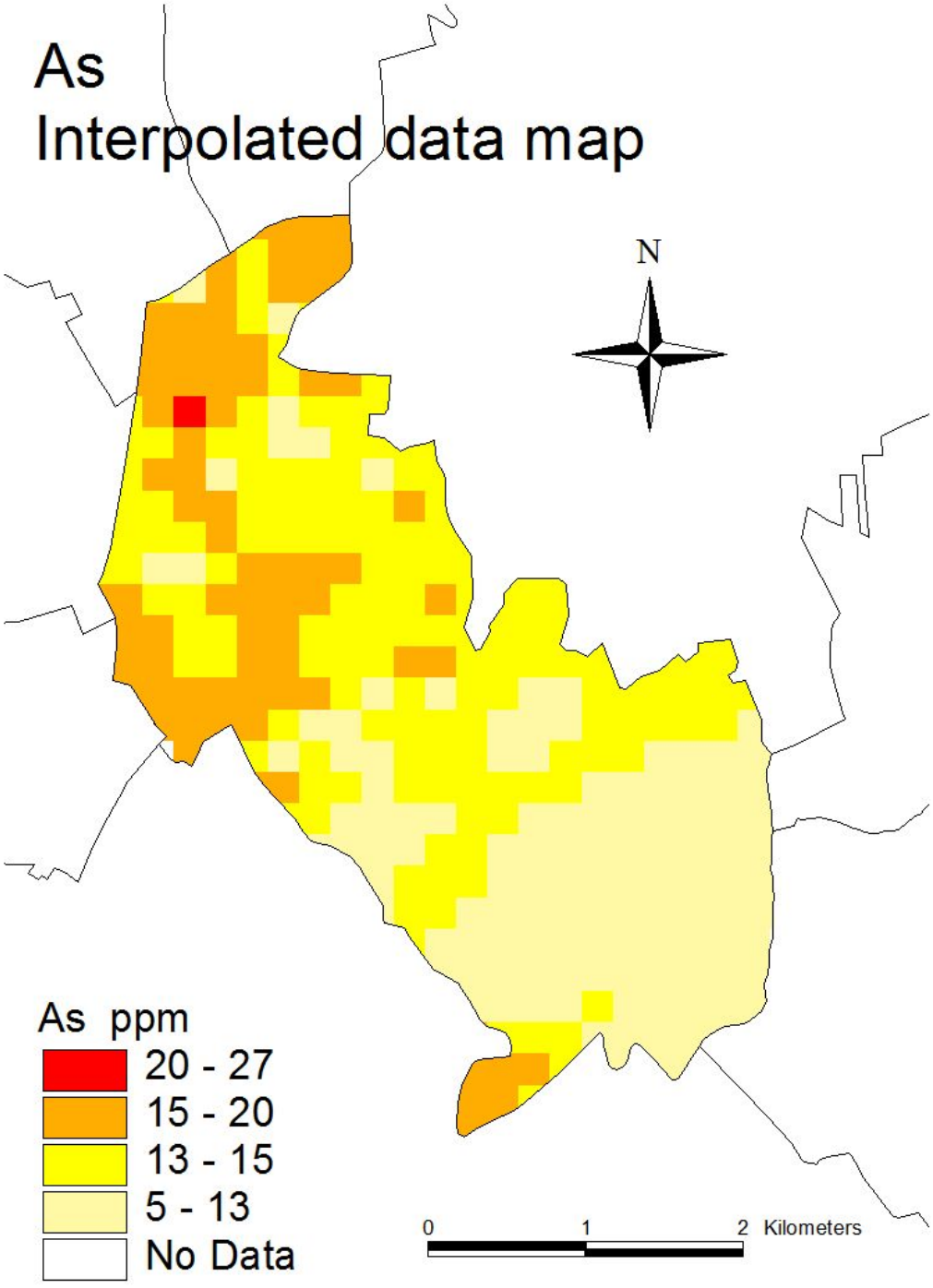

As
As
Count
Concentration
mg/kg

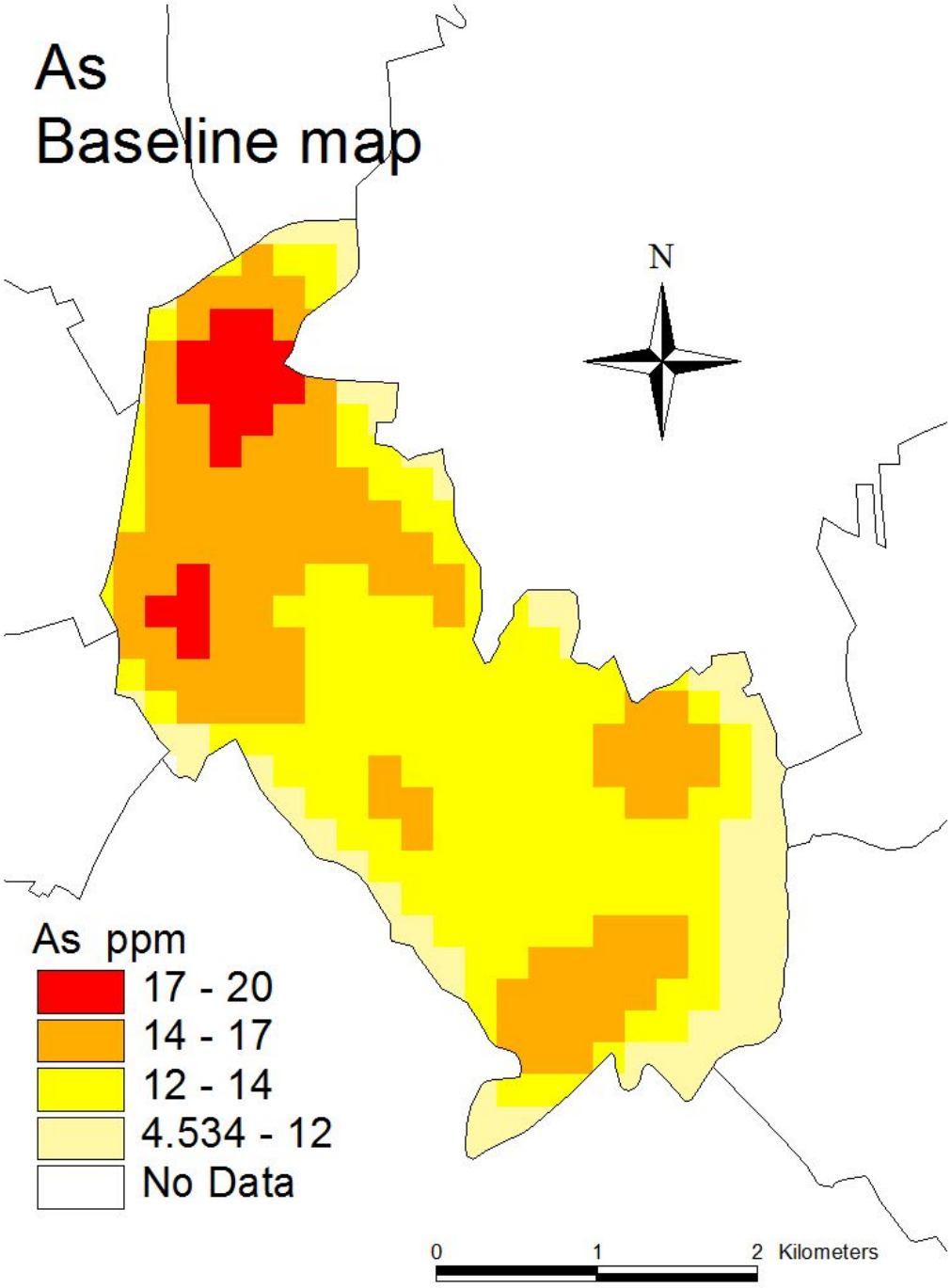

As
As
mg/kg
Percent
Concentration (log10)


As
Concentration
mg/kg

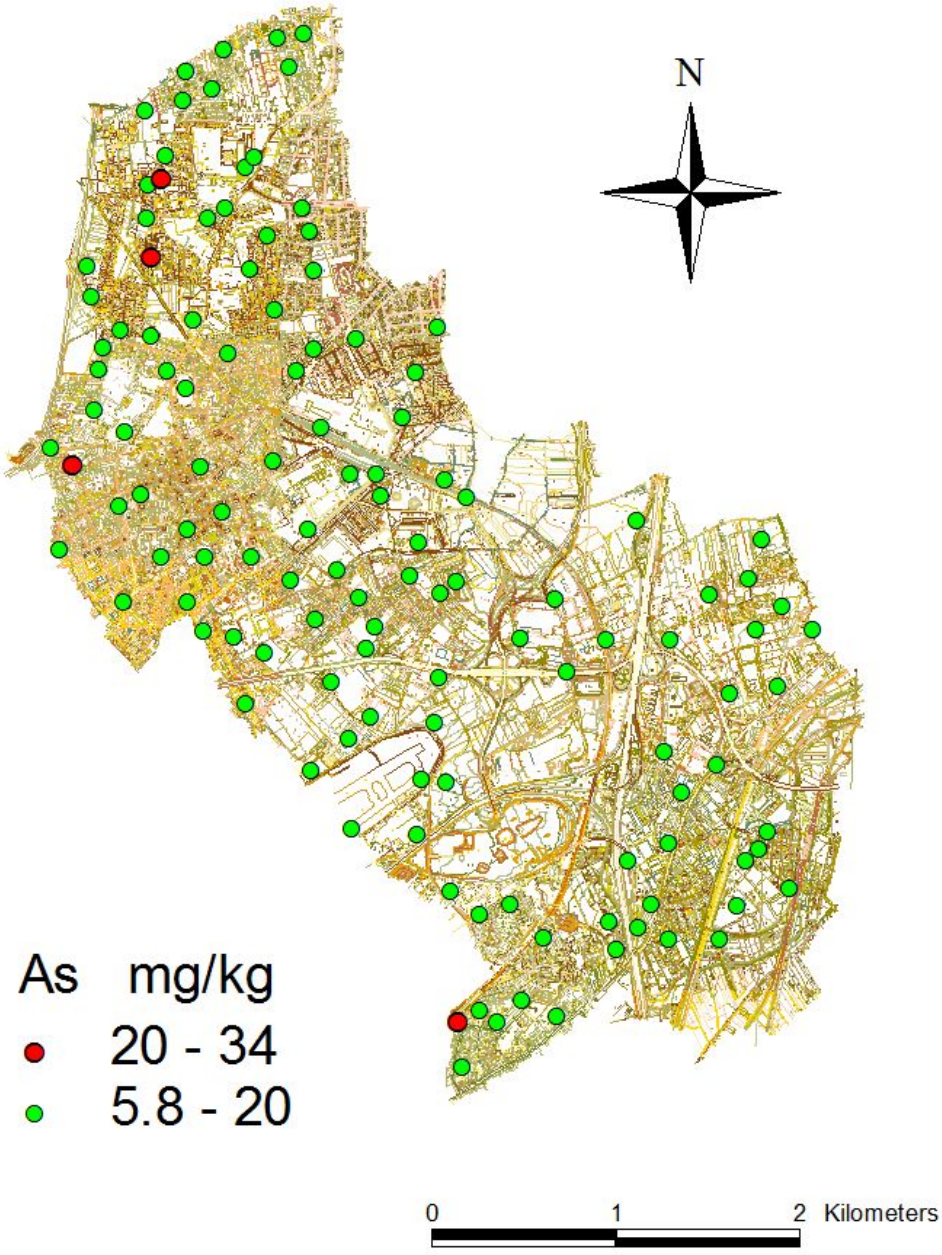
As
Dot Map




As
Interpolated data map
N
As ppm
20 - 27
15 - 20
13 - 15
5 - 13
No Data
0
1
2 Kilometers


As
Baseline map
N
As ppm
17 - 20
14 - 17
12 - 14
4.534 - 12
No Data
0
1
2 Kilometers

As
Risk map (D.Lgs. 152/06)
Residential threshold 20 mg/kg



Beryllium (Be)

Beryllium is a toxic bivalent element, with an excellent thermal conductivity; it's nonmagnetic and air oxidation resistant.

Its main uses are in beryllium-copper alloys for defense and aerospace industries, in the diagnostic X-ray detection, and in computer components production.

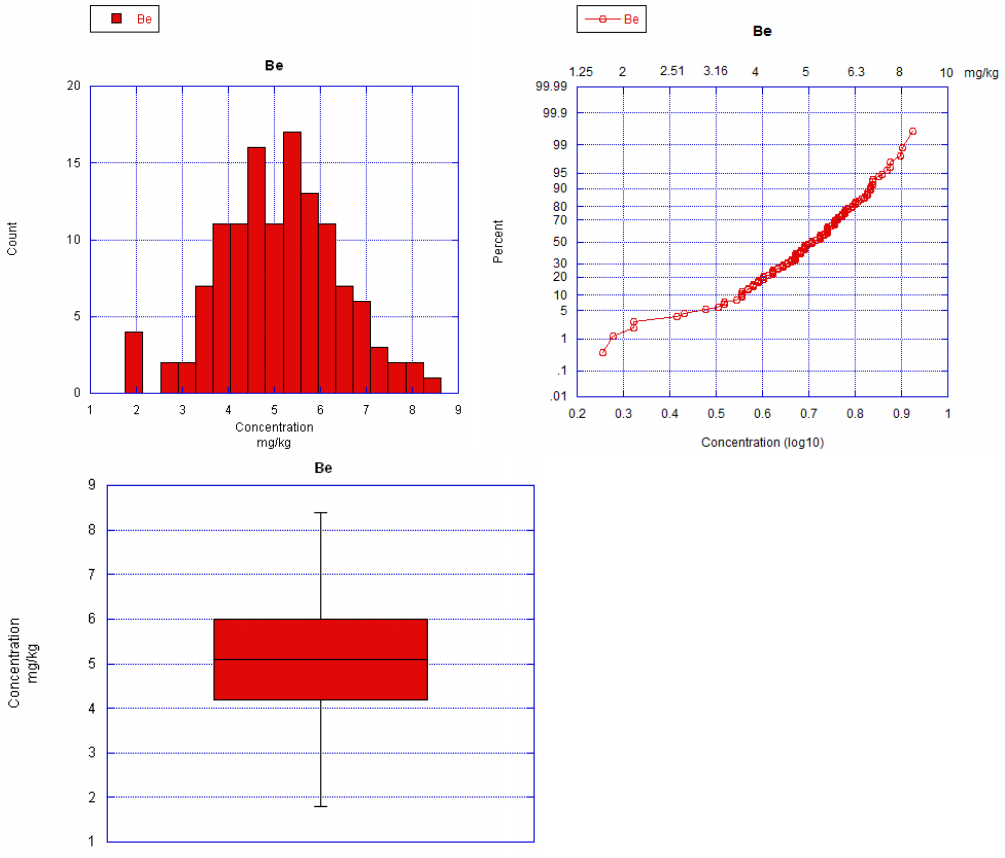
Beryllium average content in soil is 6 mg/kg; in this environmental media it's in a soluble form and can be taken from plants growing on Be-rich soils. Plants could accumulate Be contents varying between 1 and 40 mg/kg; these concentrations are too low to cause health problems to animals who eat these plants.

Beryllium added into the environment by anthropic activities is especially by industrial emissions and wastewaters disposals. In waters, through reactions, beryllium becomes insoluble and causes much less harm to organisms than water-soluble form.

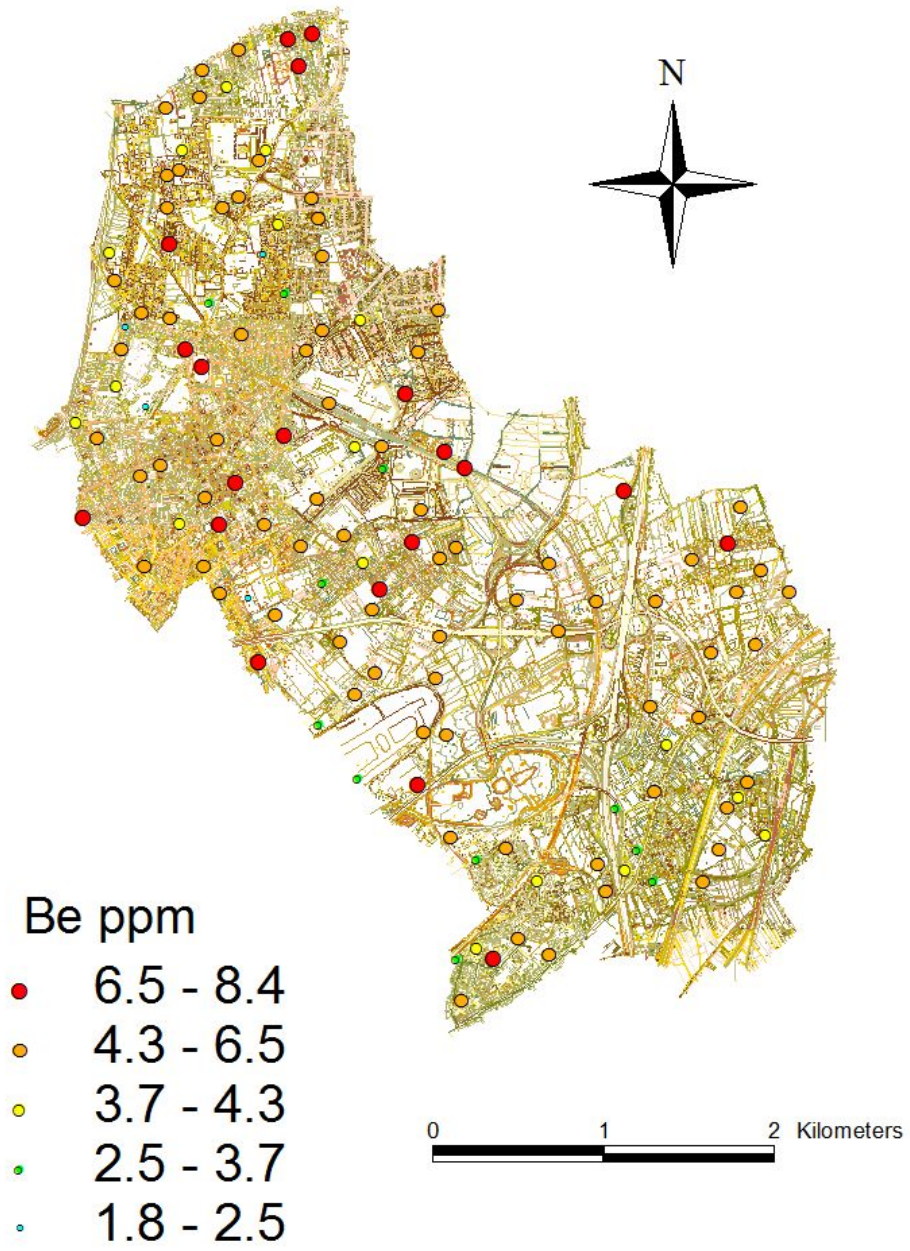
Distribution of Be concentrationts

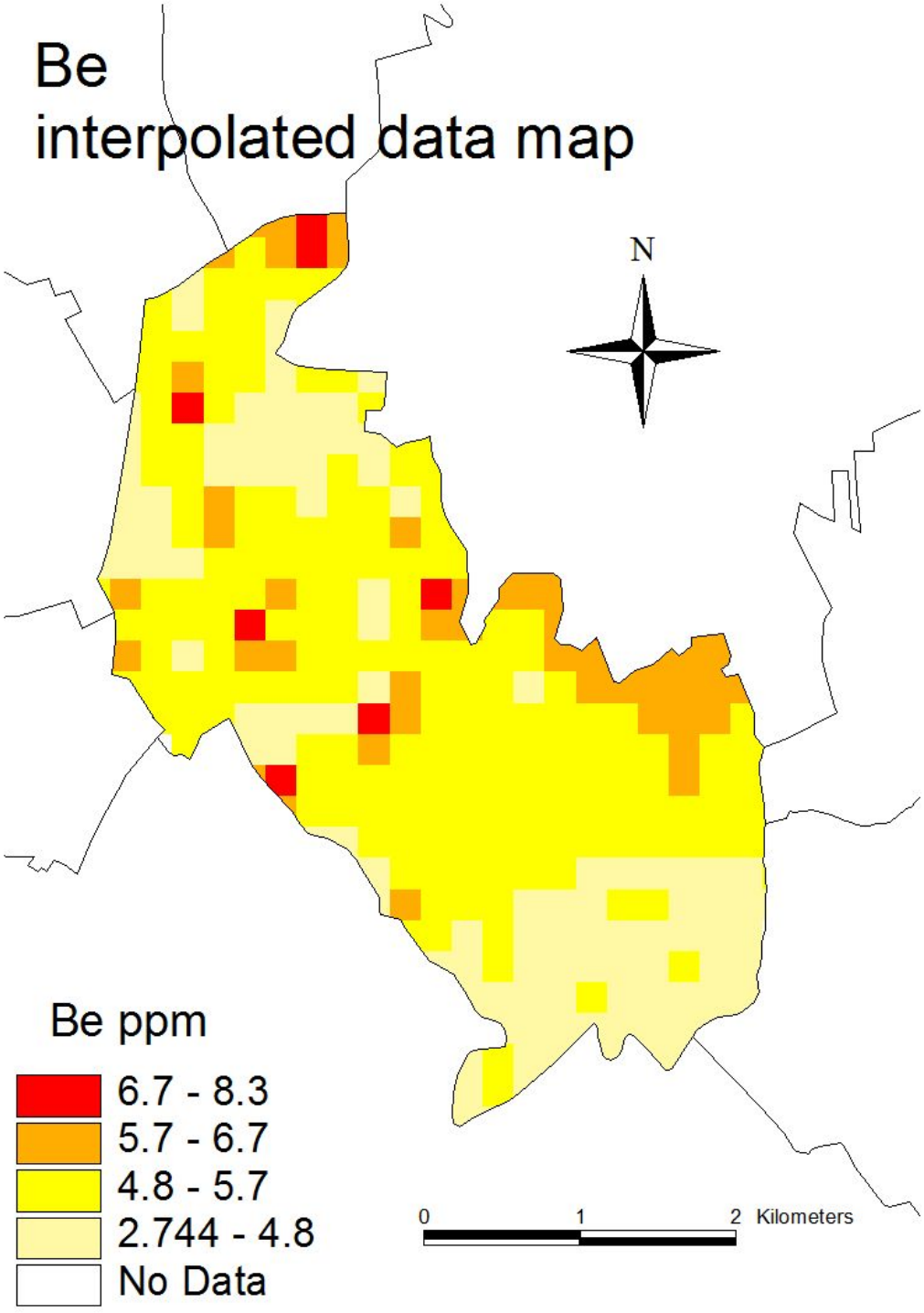
Be concentrations measured in Casoria soils shows high values (4.3 – 8.4 mg/kg) detected in several areas probably due to industrial aeronautic activities which are still present (Alenia Company and Capodichino International Airport). Baseline values are clearly influenced by anthropic activities with higher values up to 5.65 mg/kg .

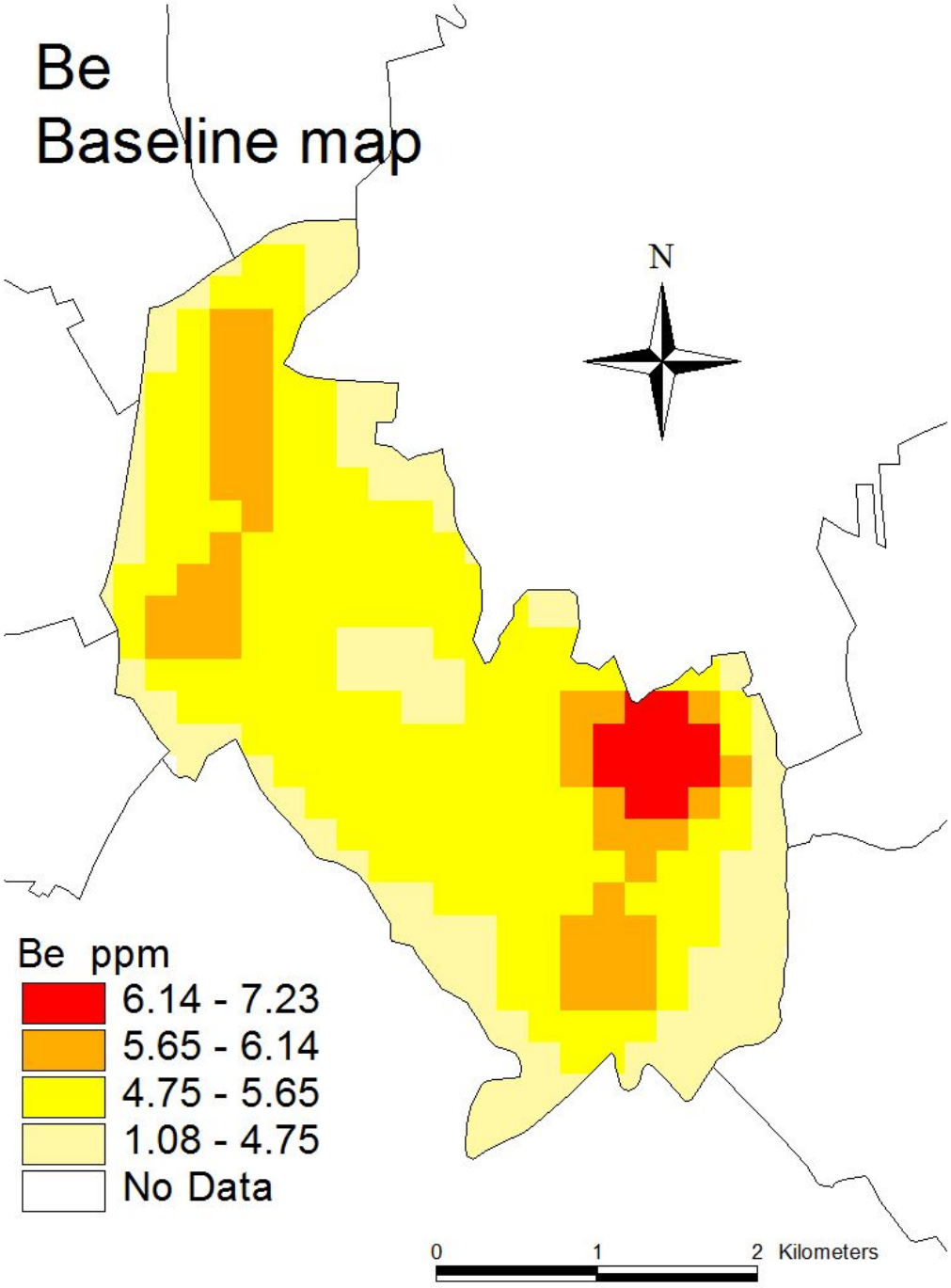
Environmental Italian law fix Be concentration limit for residential areas (2 mg/kg) and for industrial areas (10 mg/kg). Casoria Be values exceeded residential threshold in almost all the municipal area.



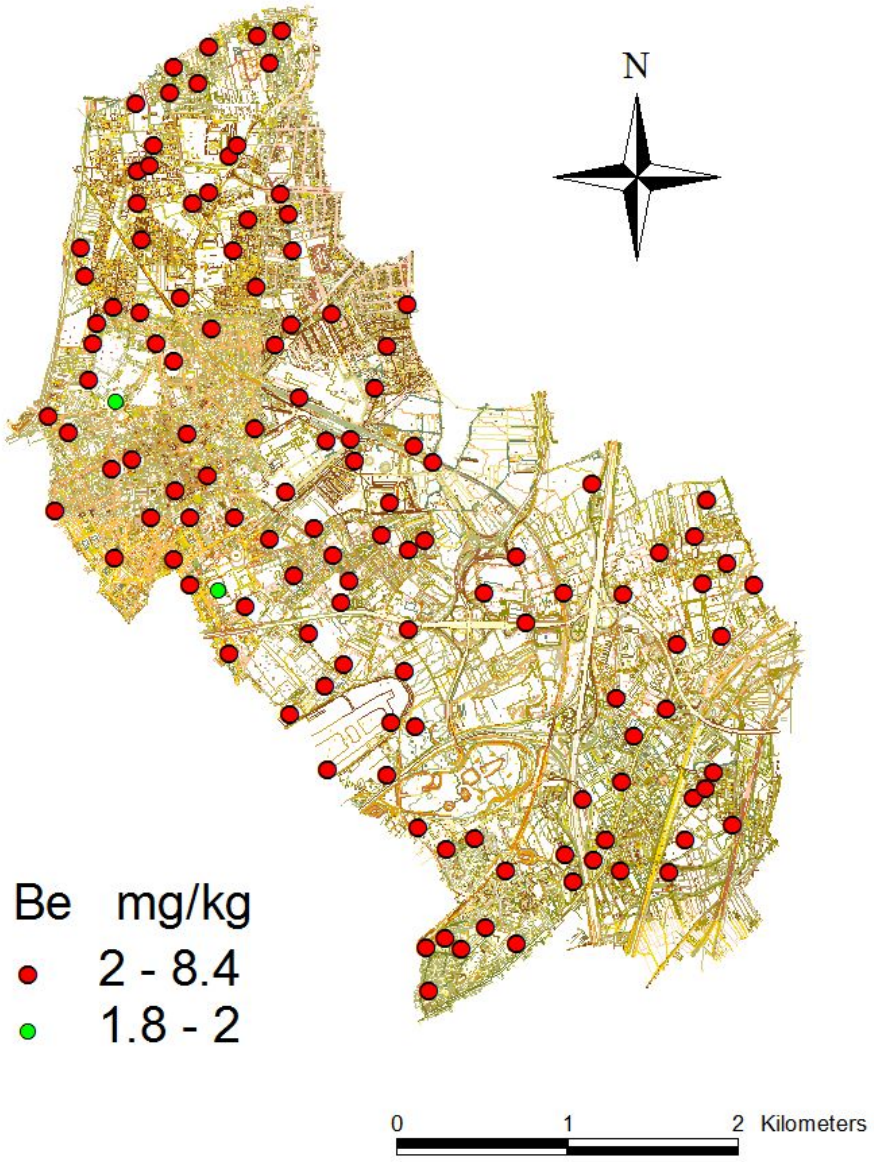
Be
Dot Map




Be
interpolated data map
N
Be ppm
6.7 - 8.3
5.7 - 6.7
4.8 - 5.7
2.744 - 4.8
No Data
0
1
2 Kilometers


Be
Baseline map
N
Be ppm
6.14 - 7.23
5.65 - 6.14
4.75 - 5.65
1.08 - 4.75
No Data
0
1
2 Kilometers

Be
Risk map (D.Lgs. 152/06)
Residential threshold 2 mg/kg



Cadmium (Cd)

Cadmium is a metal with physical and chemical properties similar to those of zinc. A large amount of produced cadmium is used in Ni-Cd batteries, the remaining is mainly used for pigments, coatings and plating, and as stabilizers for plastics.

Most of the produced Cd is a by-product of sphalerite (ZnS), in which CdS is present as a significant impurity; for this reason the major Cd mining districts are those associated with zinc; its main producing countries are: Canada, USA, Australia, Mexico, Japan and Peru.

Most of the cadmium found in the environment derives from natural events such as rock's weathering, forest fires and volcanoes. Cadmium is also a by-product of zinc, lead and copper extraction.

Food is the main Cd source for humans; aliments Cd-rich, such as mushrooms, cocoa powder, mussels and shellfish, can increase Cd concentrations in the human organism. People who smoke are particularly exposed to high Cd contents; other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air.

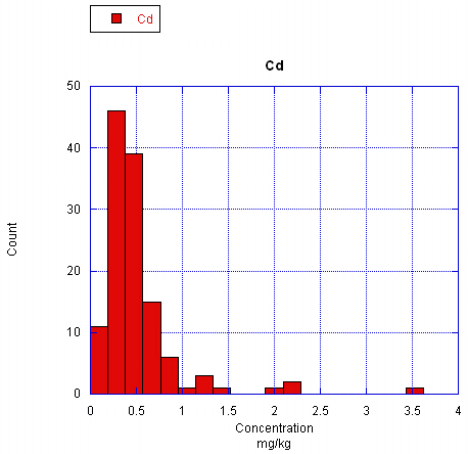
Breathing in cadmium can cause lungs damages and also lead to death. Other health effects that can be caused by cadmium are: stomach pains, bone fracture, reproductive failure, possibly DNA damage or cancer development.

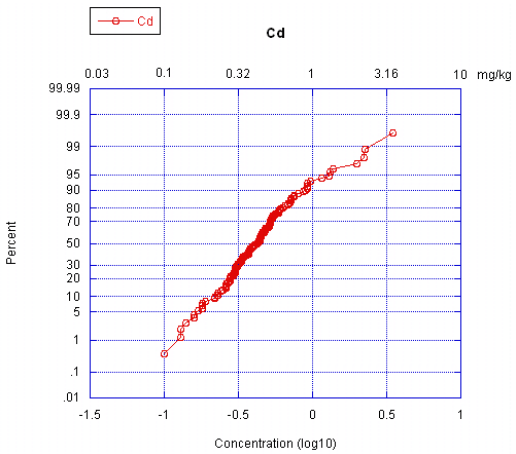
Cadmium may enter in soils and air through industries wastes and combustion of fossil fuels. Artificial phosphate fertilizers are another important Cd source in the environment; the use of such fertilizers increase Cd contents in both soils and waters. Acidified soils promote cadmium uptake by plants and, consequently, Cd absorbed by animals and humans through food increases. Earthworms and other essential soil organisms are very likely to be poisoned by cadmium even at very low concentrations. In aquatic environment Cd can bio-accumulate in mussels, oysters, shrimps, lobsters and fish. Health problems occurred in animals eating or drinking cadmium is the increasing blood-pressure, liver disease and nerve or brain damage.

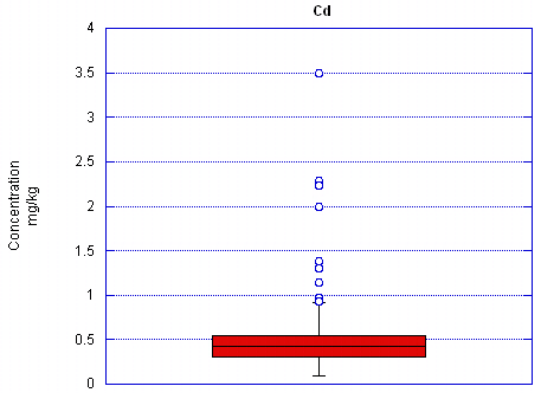
Distribution of Cd concentrationts

Cd distribution is strongly influenced by the anthropogenic activities in the territory, especially in the Casoria north-western area on the Naples border (high urbanized and industrializated sector). In these areas, values reach up to 3.5 mg/kg. Results in most of the Comune di Casoria territory are characterized by baseline values between 0.1 and 0.7 mg/kg. These values, similar to Neapolitan provincial area can be assumed to represent the natural background values of soils of Neapolitan volcanic area (Cicchella et al. 2005).

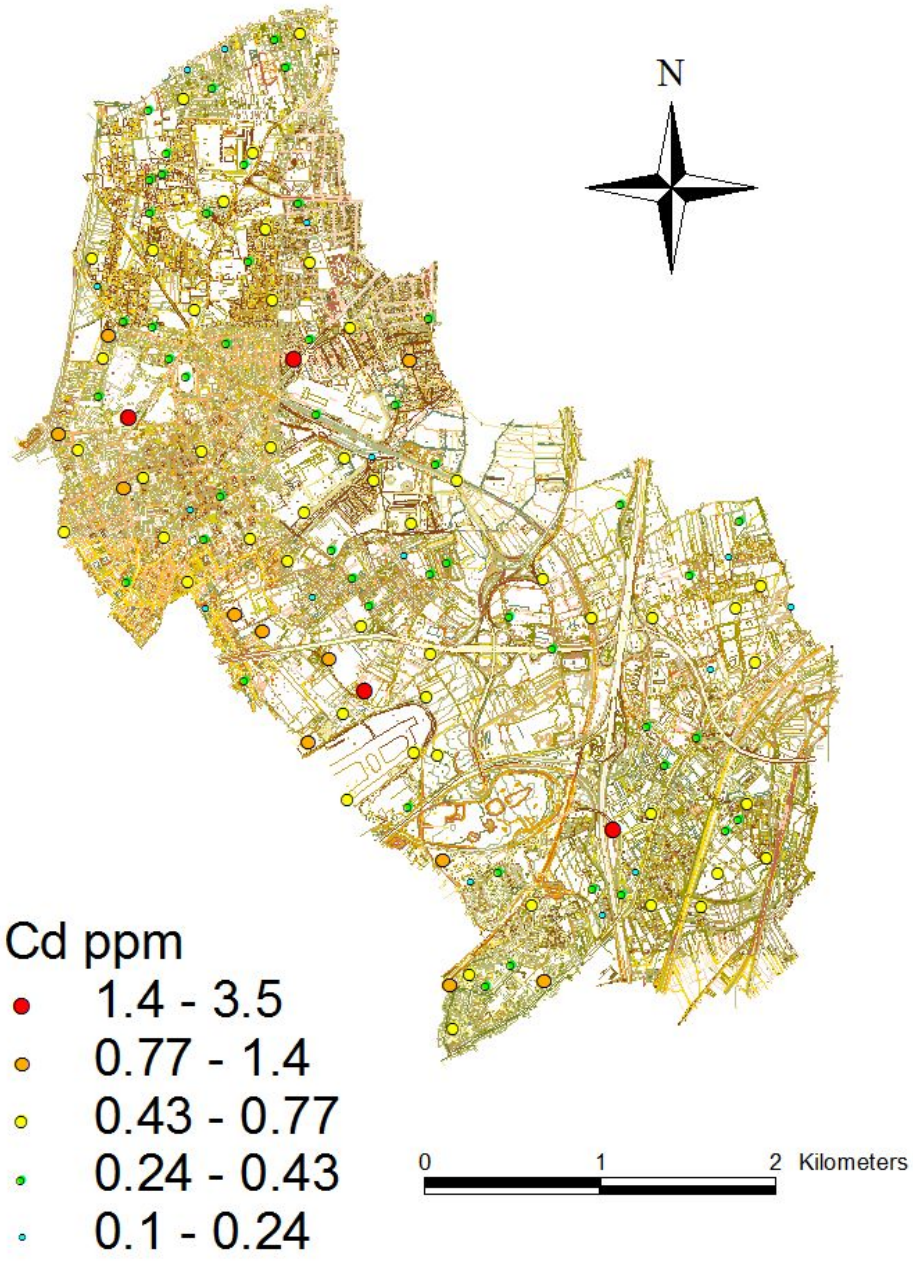
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (2 mg/kg) and for industrial soils (15 mg/kg). Casoria soils Cd concentrations is higher than D.Lgs 152/06 residential threshold in 4 samples closer the principal ex-industrial areas and airport.

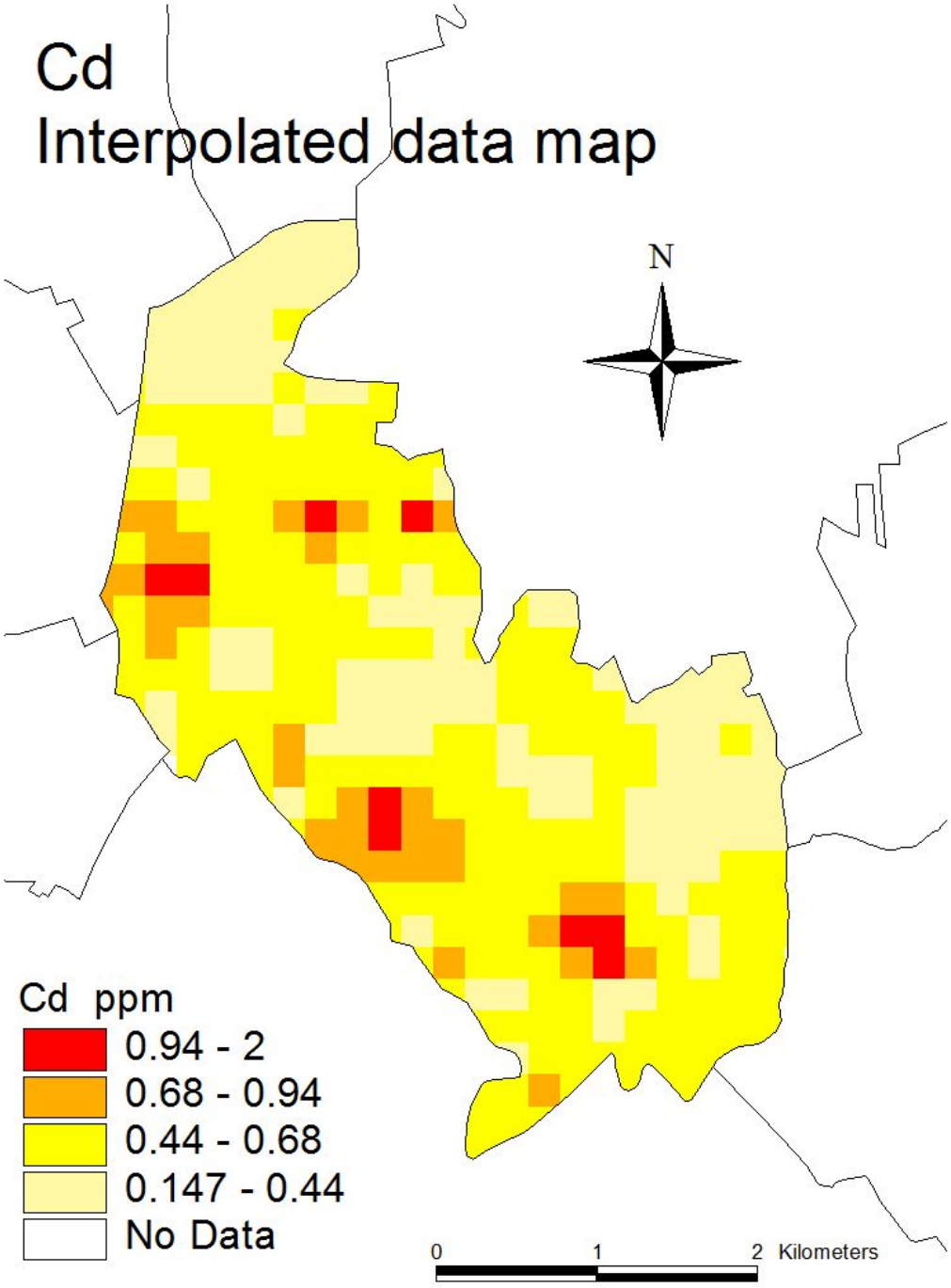

Cd
Cd
Count
Concentration
mg/kg

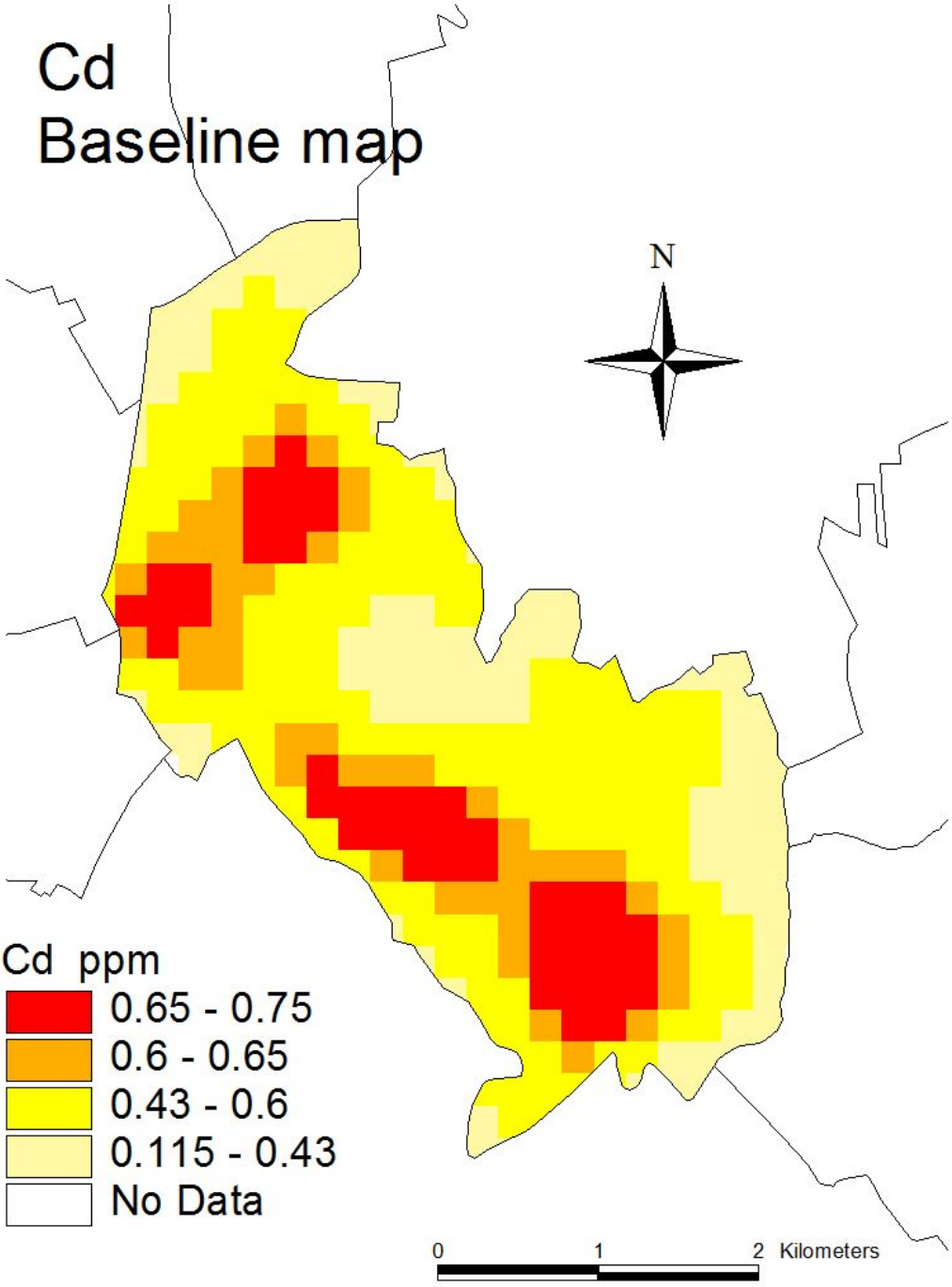

Cd
Cd
mg/kg
Percent
Concentration (log10)


Cd
Concentration
mg/kg

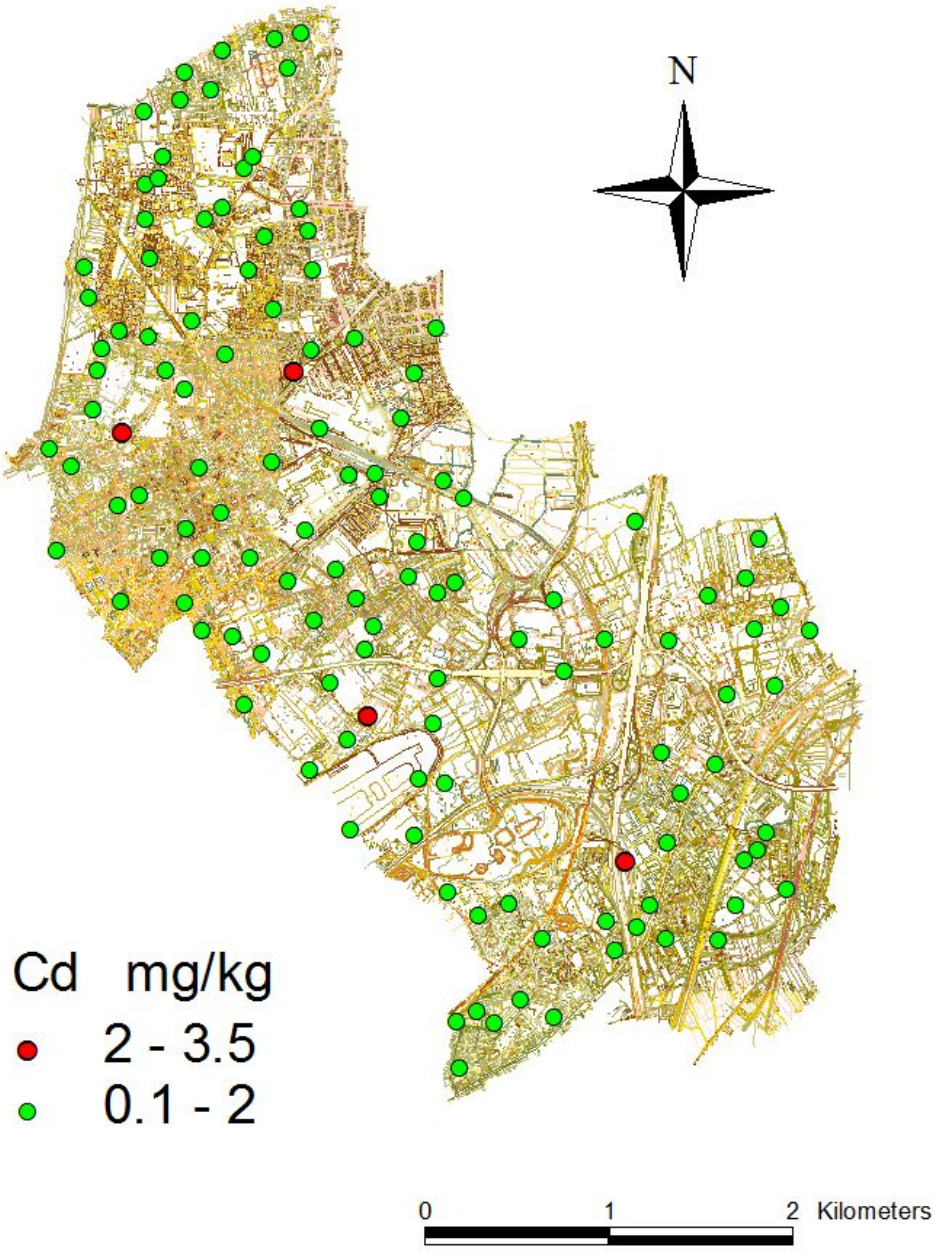
Cd
Dot Map




Cd
Interpolated data map
N
Cd ppm
0.94 - 2
0.68 - 0.94
0.44 - 0.68
0.147 - 0.44
No Data
0
1
2 Kilometers


Cd
Baseline map
N
Cd ppm
0.65 - 0.75
0.6 - 0.65
0.43 - 0.6
0.115 - 0.43
No Data
0
1
2 Kilometers

Cd
Risk map (D.Lgs. 152/06)
Residential threshold 2 mg/kg



Cobalt (Co)

Cobalt is a hard ferromagnetic element with physical properties very similar to those of iron and nickel.

It doesn't occur as a free metal and most of the times is obtained as a by-product of copper and nickel mining activities. The main minerals in which is found are cobaltite, erythrite, glaucodot, and skutterudite. The countries with the major cobalt production: are the Democratic Republic of the Congo, Zambia, China, Australia and Russia.

Cobalt is used in the petroleum and chemical industries, in many alloys, in paints, inks and as Cobalt blue for craftworks and paintings. Although Cobalt is an essential element for human health (it's a part of vitamin B12), too high concentrations may be harmful. Breathing in high cobalt contents could cause lung problems, such as asthma and pneumonia. This mainly occurs with people that work with cobalt.

Plants grown up on contaminated soils tend to accumulate cobalt in fruits and seeds, thus helping the transmission of cobalt from plants to upper levels of the biological cycle. By the way cobalt is not known to bio magnify up the food chain and, because of this, fruits, vegetables, fish and other animals we eat will usually do not contain very high amounts of cobalt.

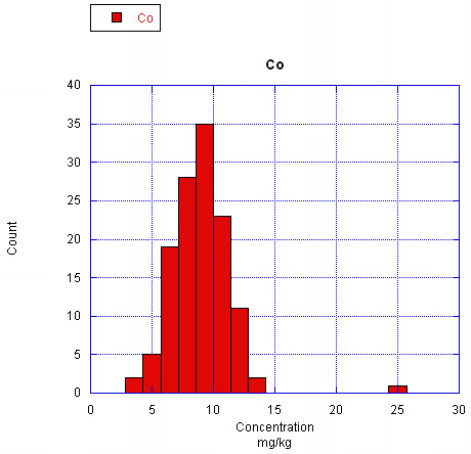
Harmful soils are those near mining and melting facilities because they may contain very high amounts of cobalt. In this case the uptake by humans through eating plants can cause serious health problems, such as: heart problems, vomiting and nausea, vision problems and thyroid damage.

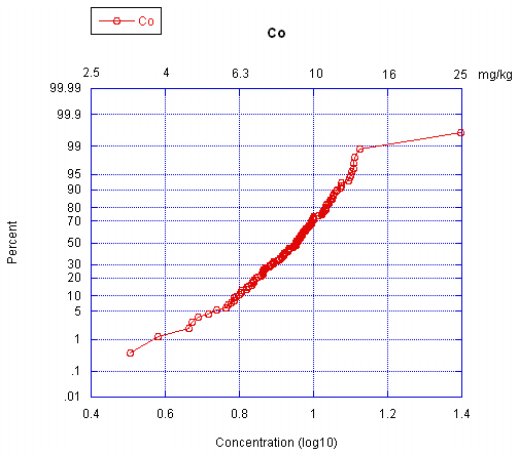
Anthropic contribution to cobalt contents in the environment are mainly related to coal combustion and mining and the production and use of cobalt chemicals.

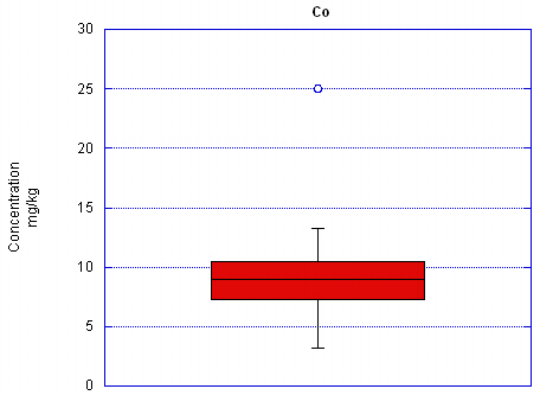
Distribution of Co concentrationts

The spatial distribution of Co values in Casoria area shows the same trends of the Neapolitan volcanic soils (higher values 25 mg/kg). The baseline values between 2 and 14 mg/kg, present in the Casoria municipality are totally coherent with Neapolitan soils background values (Cicchella et al. 2005).

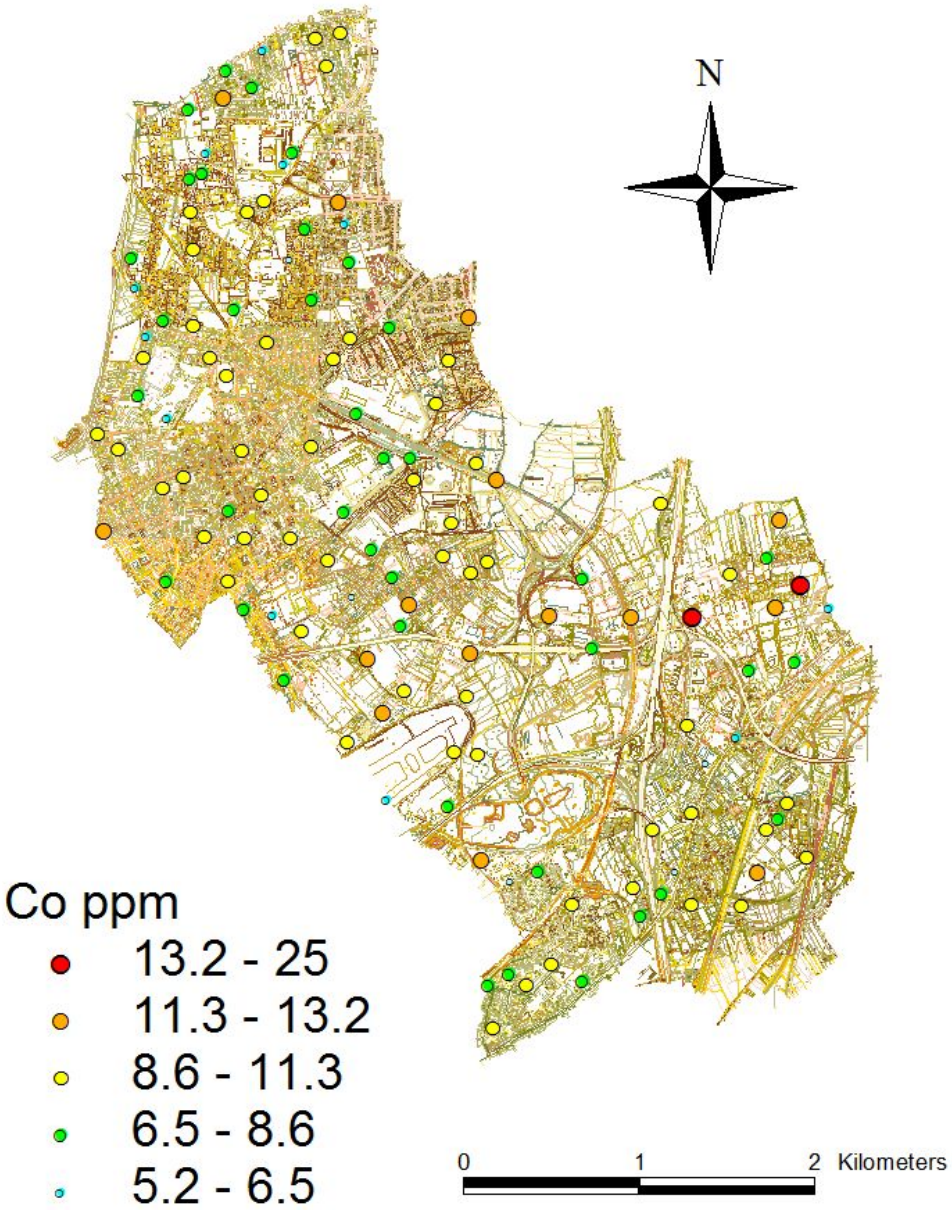
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (20 mg/kg) and industrial soils (250 mg/kg). Casoria Co soils concentration is below D.Lgs. 152/06 residential threshold excepted for 1 sample in the southern sector closer the highway.

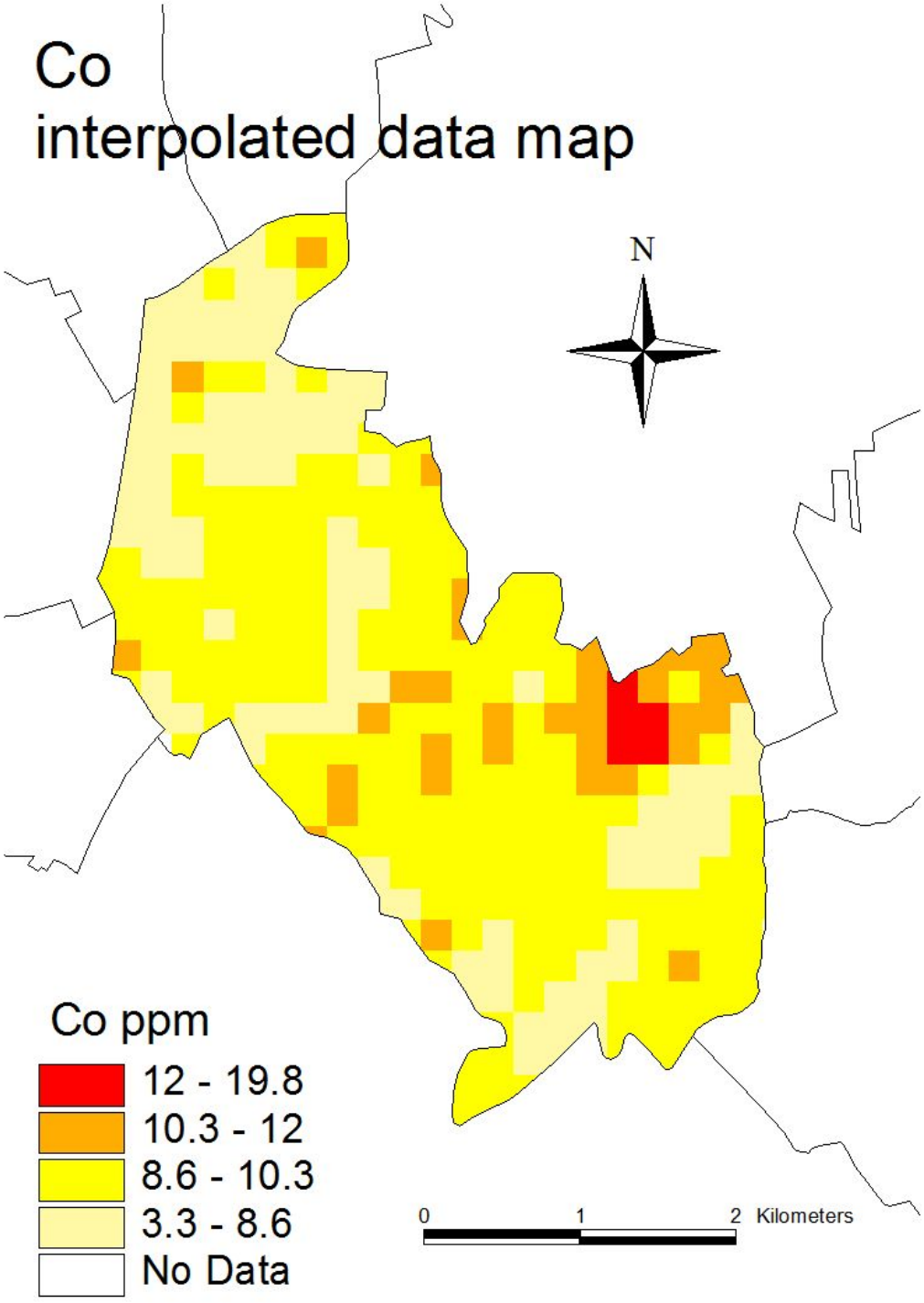

Co
Co
Count
Concentration
mg/kg

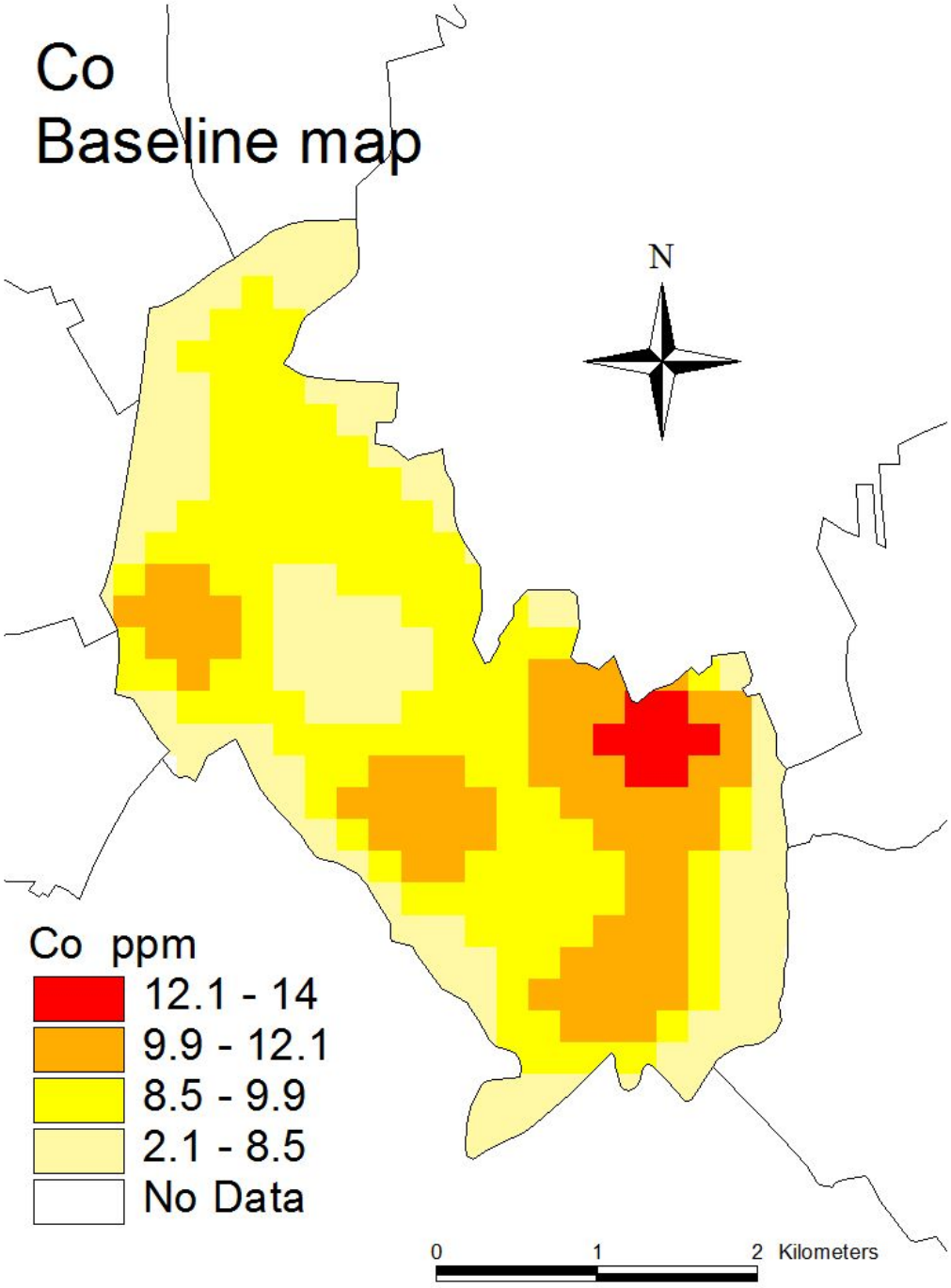

Co
Co
2.5
4
6.3
10
16
25
mg/kg
Percent
Concentration (log10)


Co
Concentration
mg/kg

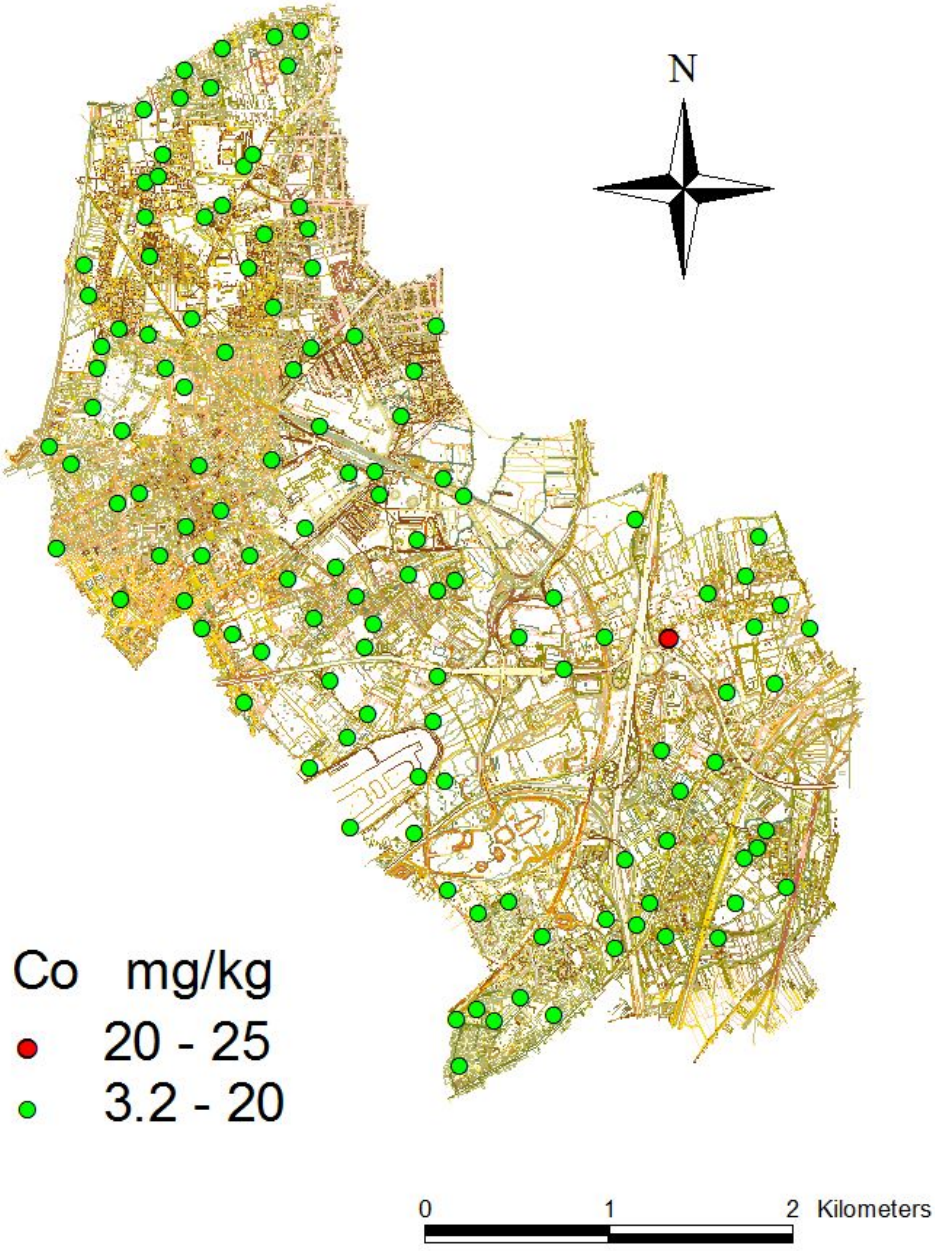
Co
Dot Map




Co
interpolated data map
N
Co ppm
12 - 19.8
10.3 - 12
8.6 - 10.3
3.3 - 8.6
No Data
0
1
2 Kilometers


Co
Baseline map
N
Co ppm
12.1 - 14
9.9 - 12.1
8.5 - 9.9
2.1 - 8.5
No Data
0
1
2 Kilometers

Co
Risk map (D.Lgs. 152/06)
Residential threshold 20 mg/kg



Chromium (Cr)

Chromium naturally occurs with different valences; the two main forms: as Cr (III) and as Cr (VI). The first is an essential nutrient for human health, whose lack may cause diabetes, heart problems and disruptions of metabolism; the last is toxic, particularly harmful for humans and is known to cause many health problems such as lung cancer, breathing problems, ulcers and also death.

Chromium main uses are in alloys, in chrome plating and in metal ceramics. It is also used as dyes and paints, especially in the tanning of leather.

Chromium is mined as chromite ($FeCr_2O_4$) and its major mines are found in South Africa, India, Kazakhstan, Zimbabwe, Finland and Philippines. Humans can assimilate Cr through skin contact, breathing, drinking and eating, but usually, its levels in air and waters are quite low.

Leather and textile manufacturing is the main anthropic source for both trivalent and hexavalent chromium. Through these activities chromium concentrations in waters rise.

Activities such as coal combustion and waste disposal contribute to increase Cr levels in air and soils.

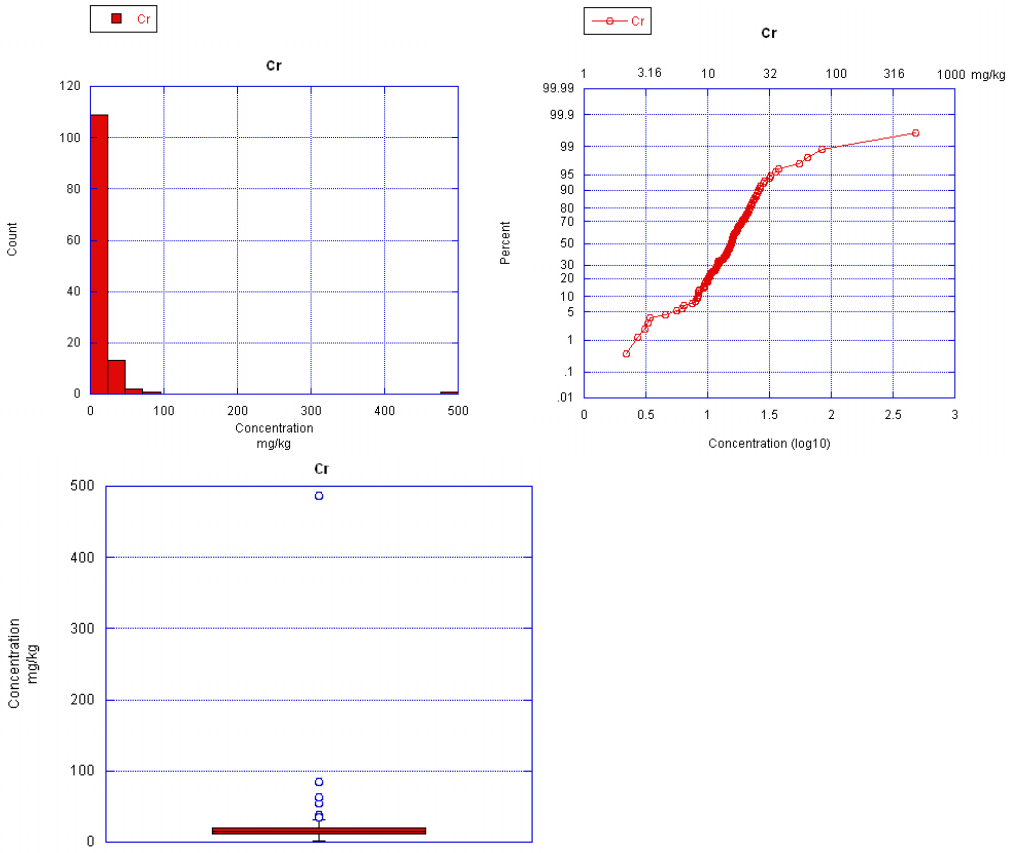
In soils chromium strongly attaches to particles and does not move towards groundwater; in waters it's absorbed on sediments and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

Distribution of Cr concentrationts

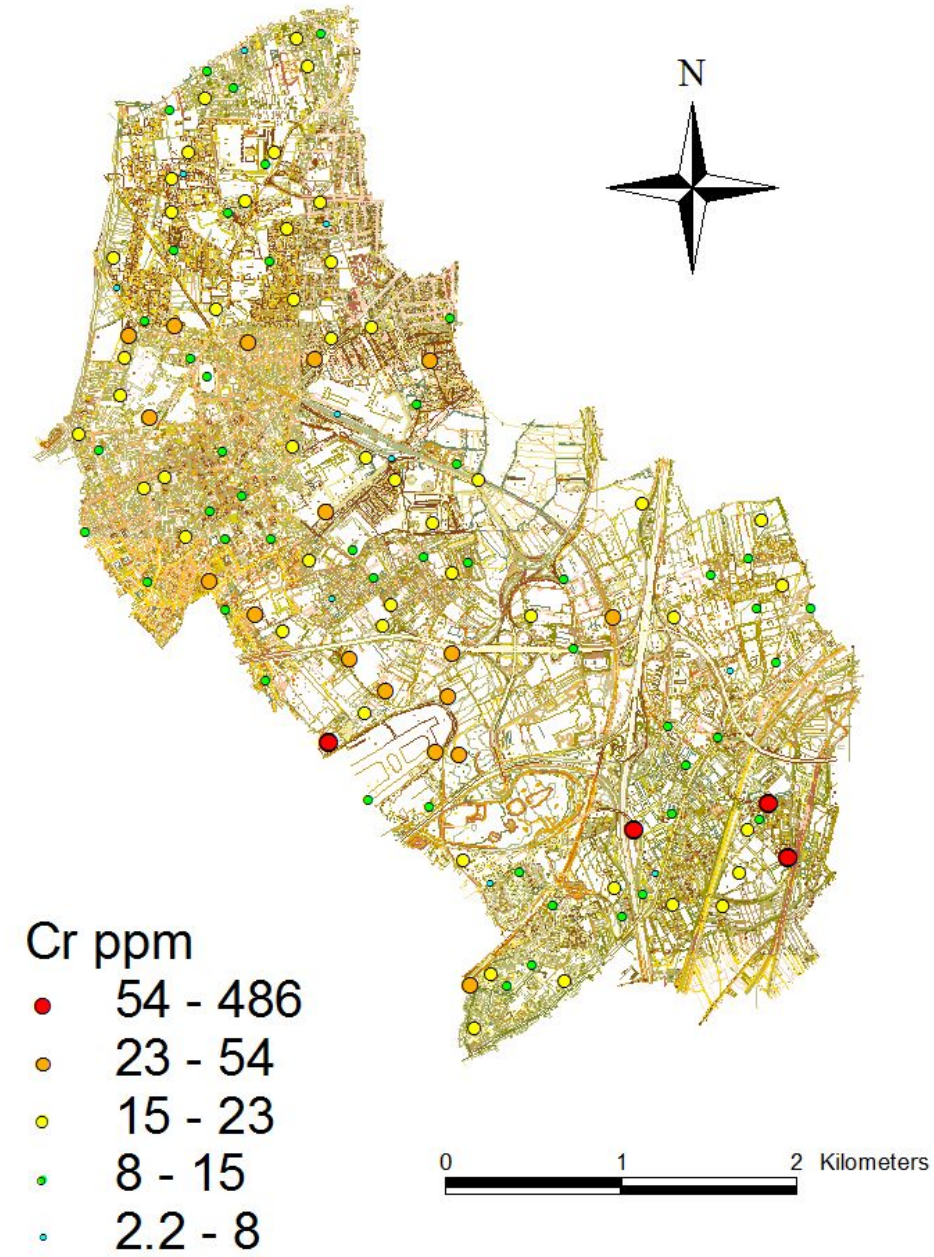
The spatial distribution of Cr values shows the highest values (up to 400 mg/kg) in the southern area of Casoria, values in the range (23-54 mg/kg) were found in the urbanized area on the border with Naples. The spatial distribution of Cr baseline values shows the highest values (25–200 mg/kg) in the southern area of Casoria. Almost of territory is characterized by values in the range 5–25 mg/kg that can be assumed to be the natural background compared to Province of Naples baseline values (Cicchella et al. 2005).

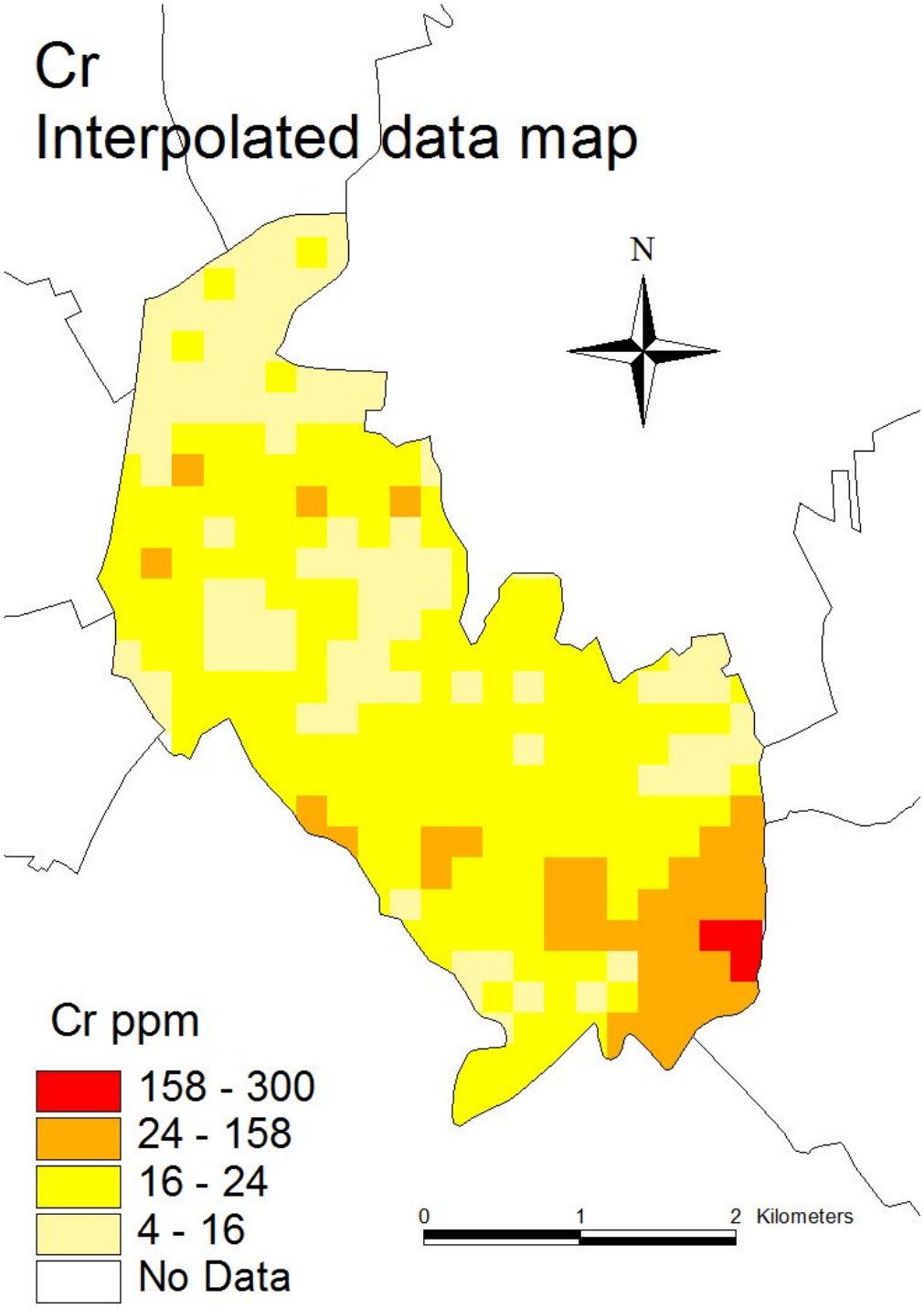
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (150 mg/kg) and industrial soils (800 mg/kg).

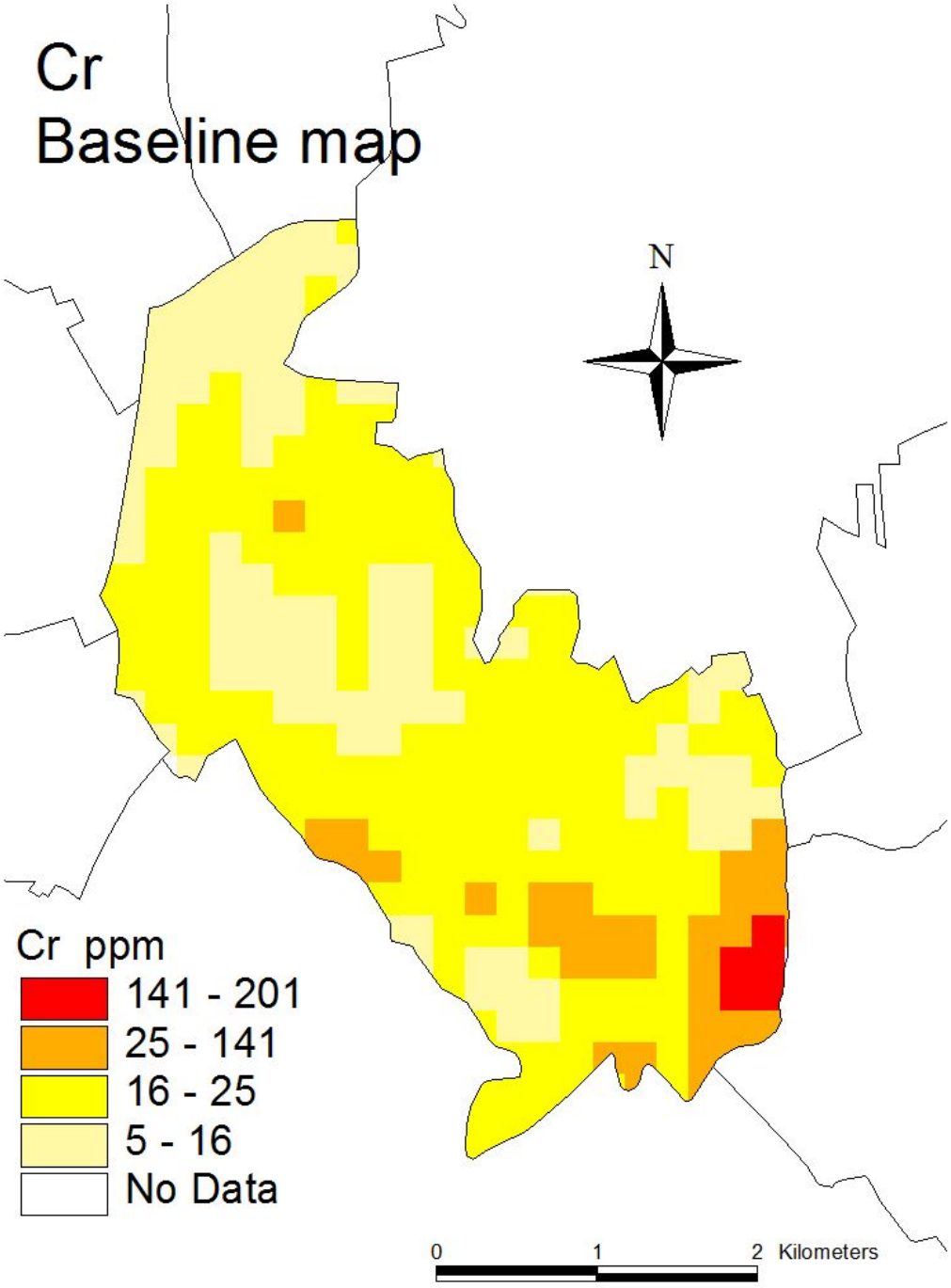
Casoria Cr soils concentration is below D.Lgs. 152/06 residential threshold excepted for 1 sample in the southern sector.


Cr
Cr
Count
Concentration
mg/kg
Cr
Cr
Percent
1
3.16
10
32
100
316
1000 mg/kg
Concentration (log10)
Cr
Concentration
mg/kg

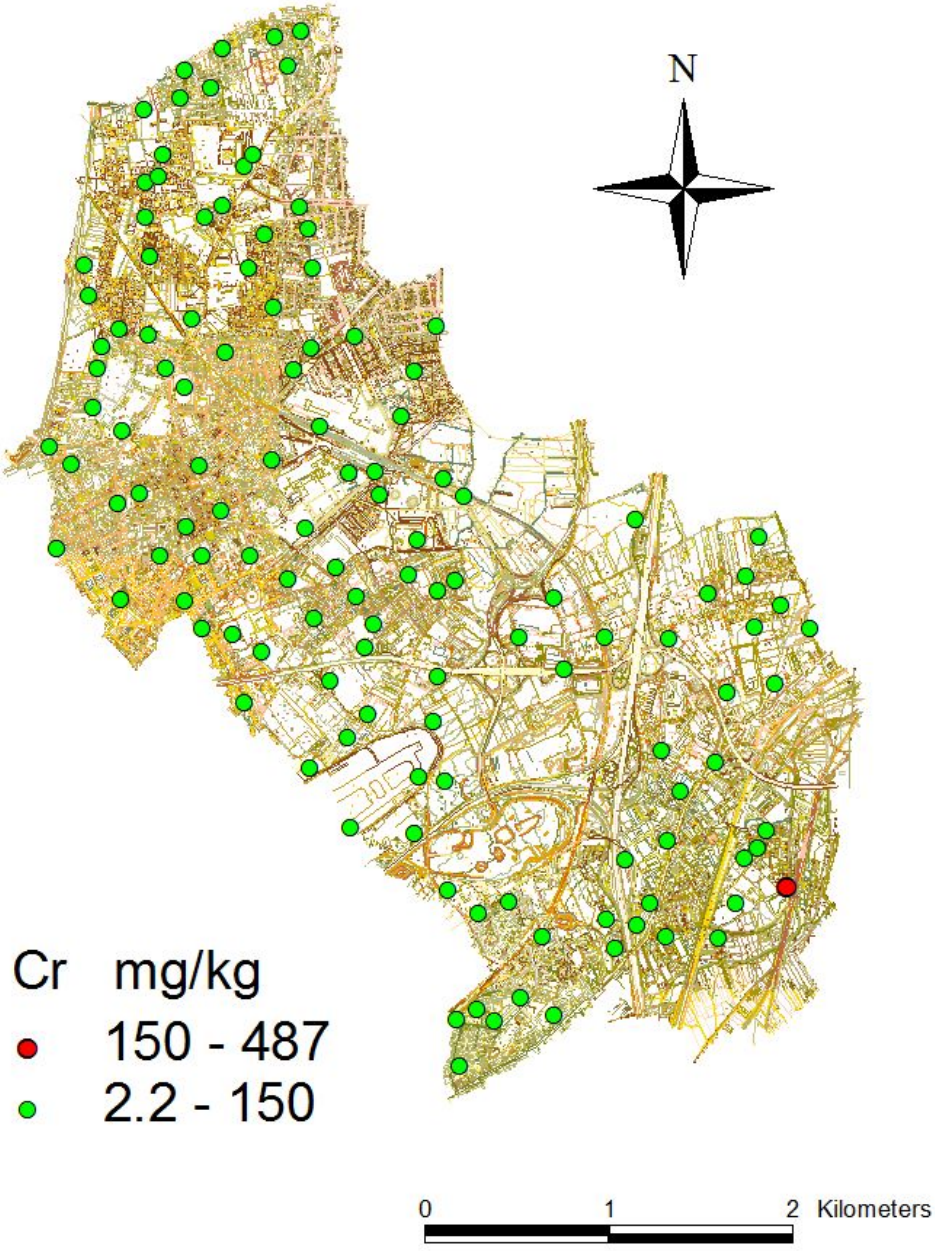
Cr
Dot Map




Cr
Interpolated data map
N
Cr ppm
158 - 300
24 - 158
16 - 24
4 - 16
No Data
0
1
2 Kilometers


Cr
Baseline map
N
Cr ppm
141 - 201
25 - 141
16 - 25
5 - 16
No Data
0
1
2 Kilometers

Cr
Risk map (D.Lgs. 152/06)
Residential threshold 150 mg/kg



Copper (Cu)

Copper is a metal with good conductivity of both heat and electricity. Because of this, copper is ideal for the production of electrical wires and other electrical equipment; other fields in which copper is widely used are roofing and plumbing constructions, and the production of alloys such as bronze, brass and cupronickel. It's also used for agricultural purposes.

The main copper ore is represented by chalcopyrite (CuFeS2) whose major mines are found in Chile, USA, Canada, Indonesia and Australia.

Copper can be found into the environment as a result of both natural sources and human activities. Natural sources of copper are forest fires, decaying vegetation and sea spray; anthropic sources are fossil fuel combustion, mining, metal production and phosphate fertilizers production.

Copper is a trace element essential for human health, but prolonged copper exposure by eating, drinking and breathing respectively food, water and air containing very high Cu contents, can cause eminent health problems. The largest harm for human health are copper water-soluble compounds that mainly occur into the environment as result of agricultural practices.

People who live in houses with copper plumbing or near smelters that process copper ore into metal are the ones mainly exposed to high and dangerous Cu concentrations.

The Wilson's Disease is the result of a chronic Cu poisoning; its characteristics are brain damage, renal disease, hepatic cirrhosis and copper deposition in the cornea.

Stomachaches, headaches, nose, mouth and eyes irritation are the consequences of prolonged Cu exposure.

In soils copper attaches to organic matter and minerals and can accumulate in plants and animals. High copper contents in soils can cause many problems to the biodiversity of that area because only a limited number of plants have a chance of survival on copper-rich soils.

Despite of this, copper-containing manures are still applied on farmlands. Furthermore copper can negatively influence microrganisms and earthworms activities in soils and the organic matter decomposition in these soils can be interrupt. Animal copper poisoning and related health problems occur in polluted farmlands; sheep are, among all the farm animals, the ones more affected by this kind of poisoning because of their low tolerance to copper.

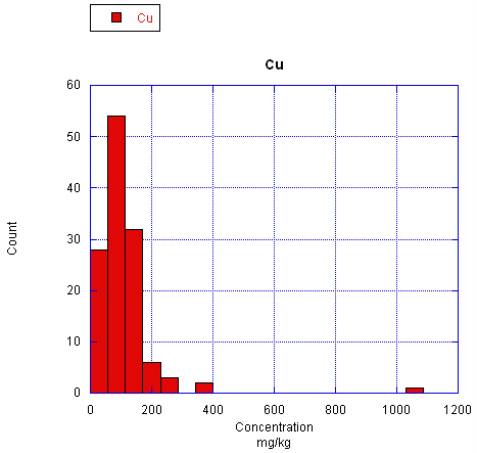
Due to its high stability in soils, copper hardly enters in groundwaters; in surface waters it's mainly transported as sludge particles or as free ions.

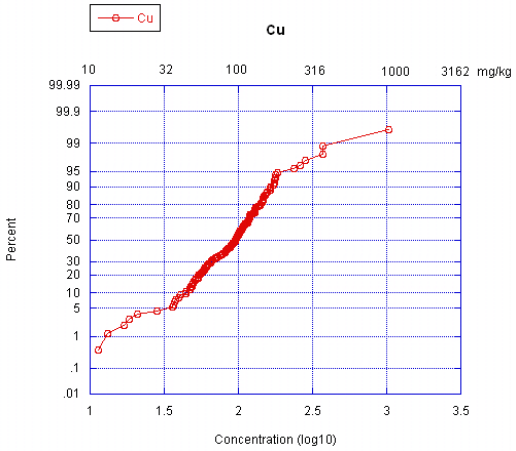
Distribution of Cu concentrationts

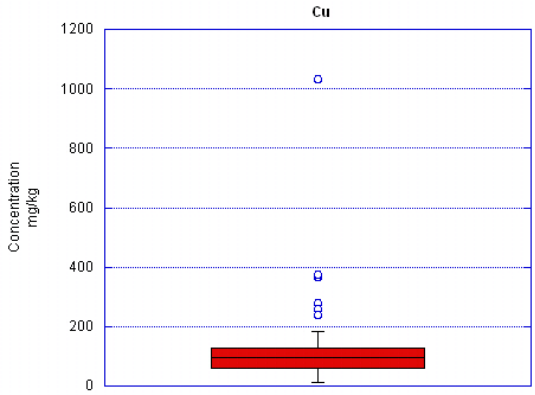
Anomaly values are present in the southern sector of Casoria and are characterized by higher values in the range 300–1000 mg/kg. Higher baseline values are in the range 129– 217 mg/kg, this values are certainly influenced by anthropogenic pollution. Copper values in the range 27–129 mg/kg, which characterize the rest of municipal soils can be assumed to be the natural background levels, as considered to Naepolitan soils baseline values (Cicchella et al. 2005).

Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (120 mg/kg) and industrial soils (600 mg/kg).

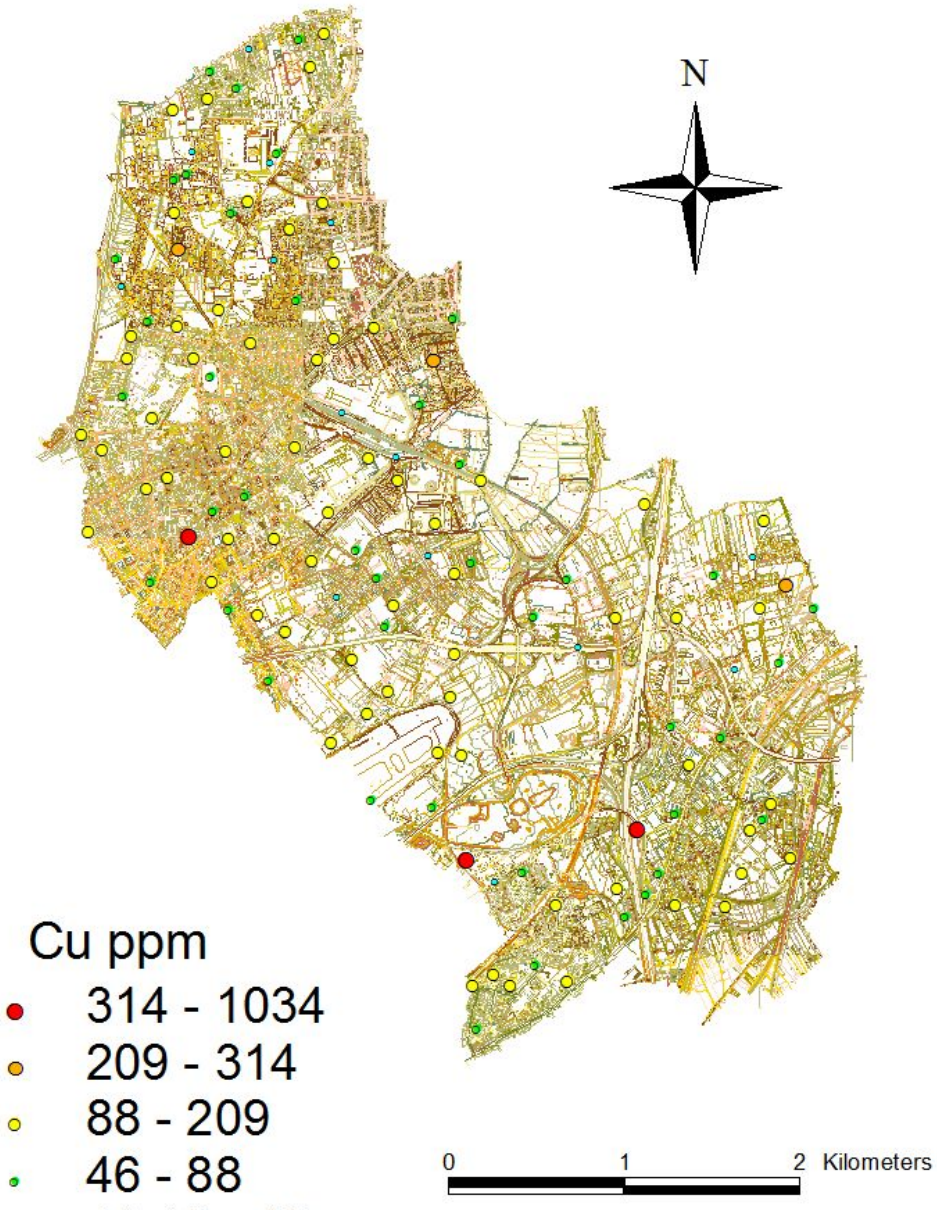
Casoria Cu soils concentration is higher D.Lgs. 152/06 residential threshold in several areas of municipal territory probably influenced by aeronautic work (Alenia Company and Capodichino International Airport) or farm activities.

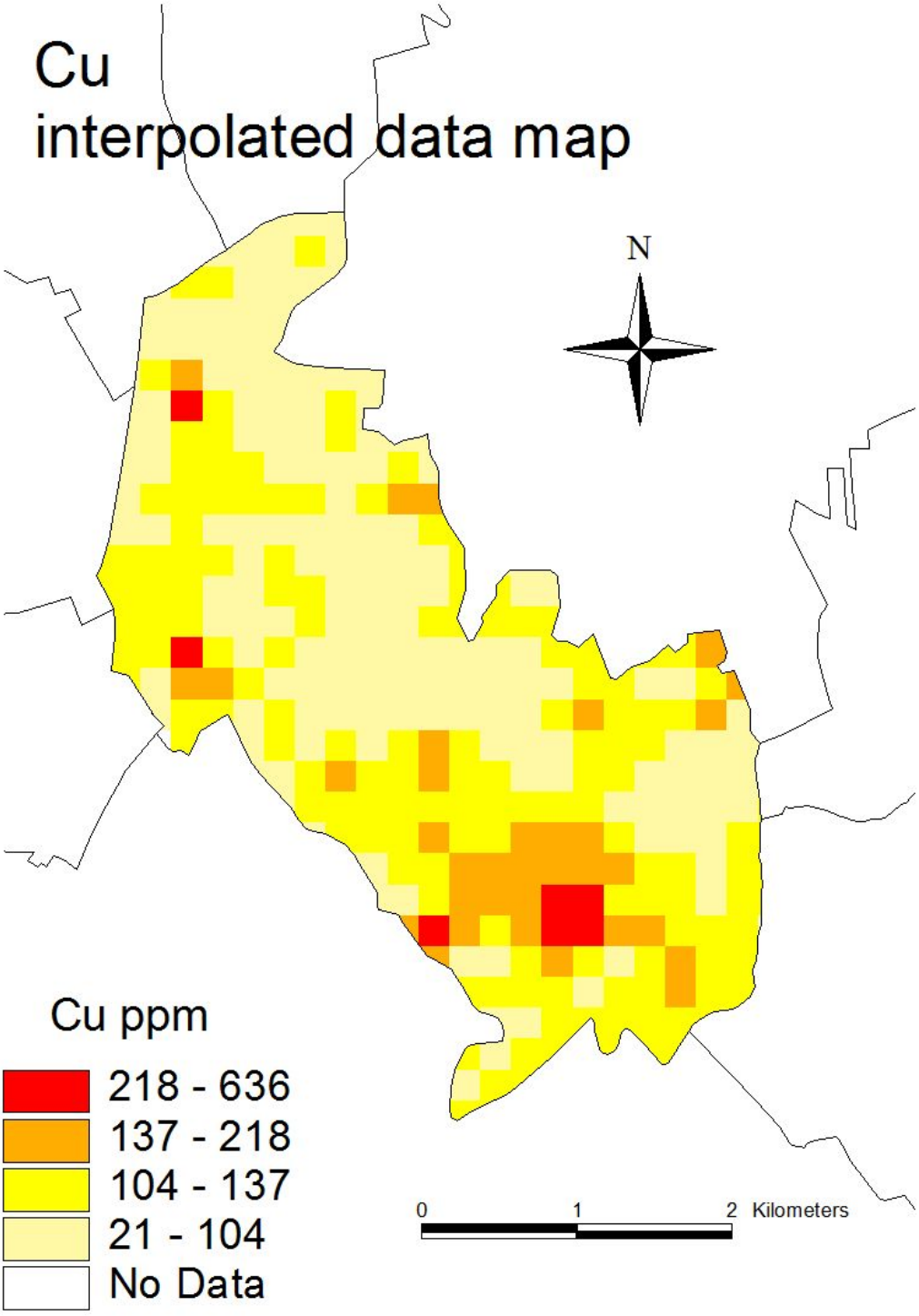

Cu
Cu
Count
0
10
20
30
40
50
60
0
200
400
600
800
1000
1200
Concentration
mg/kg

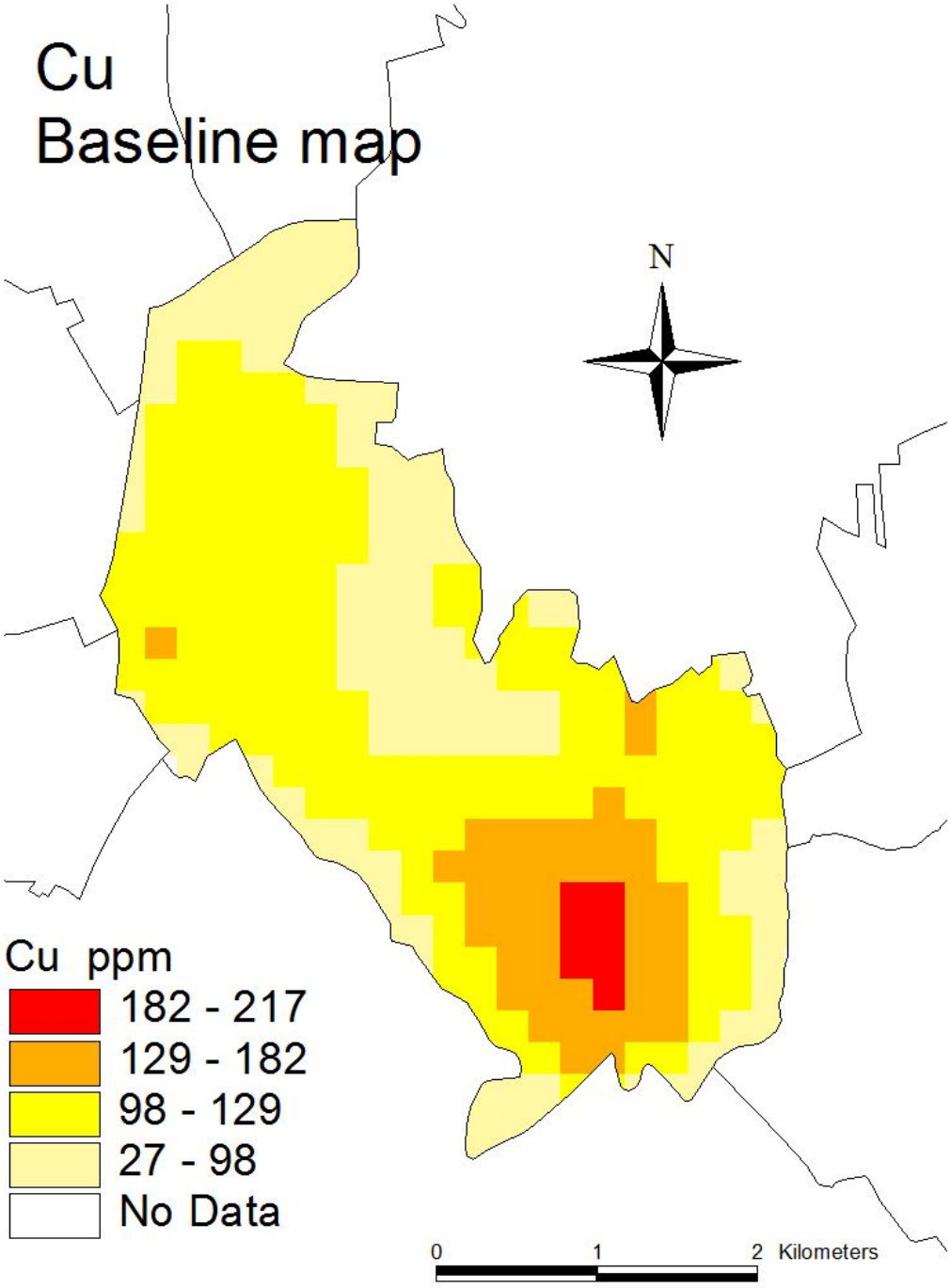

Cu
Cu
10
32
100
316
1000
3162 mg/kg
Percent
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
1
1.5
2
2.5
3
3.5
Concentration (log10)


Cu
Concentration
mg/kg
0
200
400
600
800
1000
1200

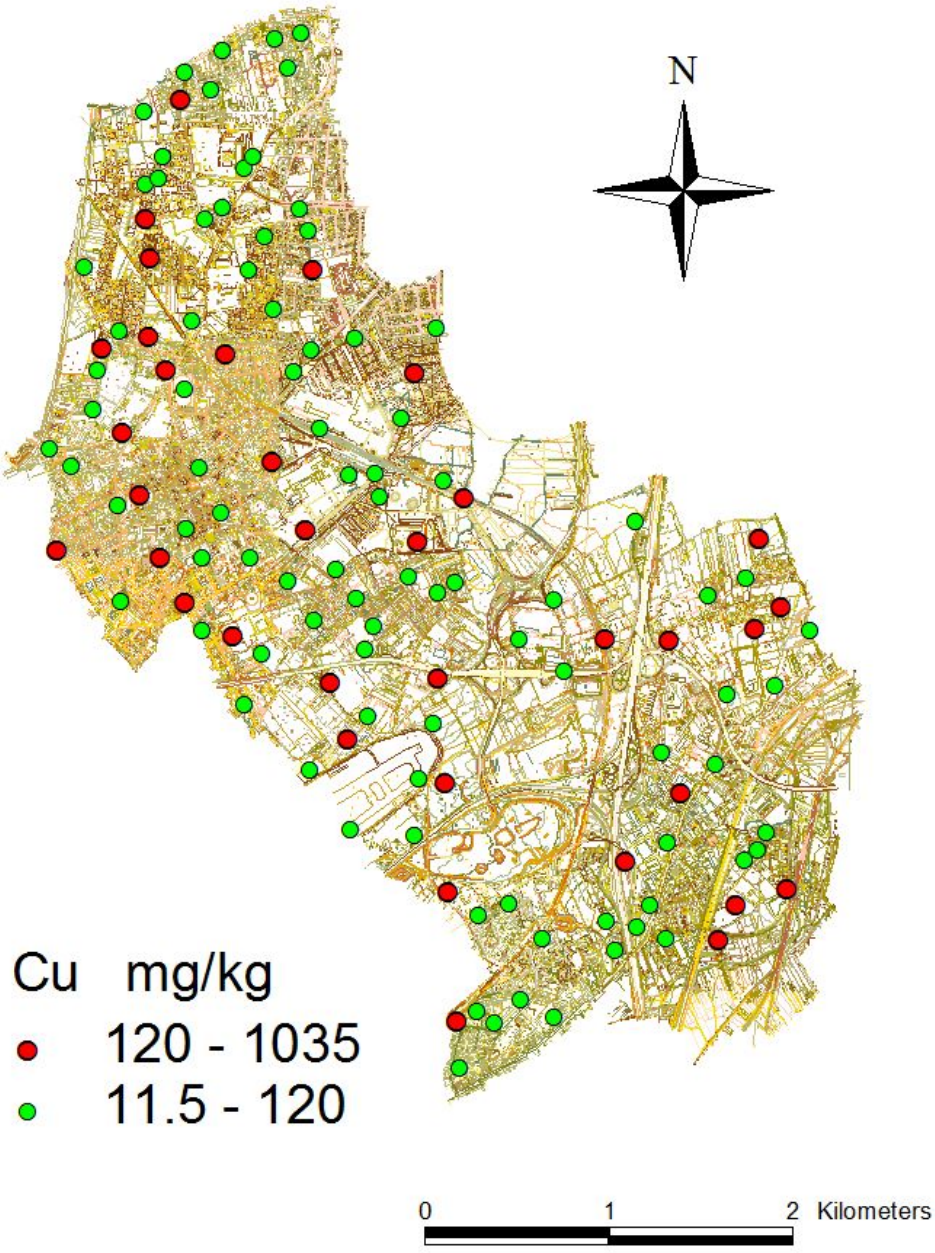
Cu
Dot Map




Cu
interpolated data map
N
Cu ppm
218 - 636
137 - 218
104 - 137
21 - 104
No Data
0
1
2 Kilometers


Cu
Baseline map
N
Cu ppm
182 - 217
129 - 182
98 - 129
27 - 98
No Data
0
1
2 Kilometers

Cu
Risk map (D.Lgs. 152/06)
Residential threshold 120 mg/kg



Mercury (Hg)

Mercury is also known as quicksilver and is a heavy, liquid metal. Its alloys with metals, such as gold, silver, and tin are called amalgams.

Mercury is a metal with a high density and a high rate of thermal expansion; due to these characteristics it's widely used in the production of manometers, barometers and thermometers. Mercury is also widely used in the chemical separation of gold from its ore, thanks to its ease in amalgamating with it. Mercury compounds have many uses: from medicine to insecticides, from disinfectants to rat poisons.

The main mercury ore is cinnabar (HgS); the main production countries are Spain, Russia, Italy, China and Slovenia.

Mercury is naturally present into the environment as a result of weathering of minerals in soils and rocks. Anthropogenic Hg is mainly released into air, through fossil fuel combustion, mining, smelting and solid waste combustion. Mercury release in soils and waters can be caused by industrial wastewater disposal or by the use of agricultural fertilizers.

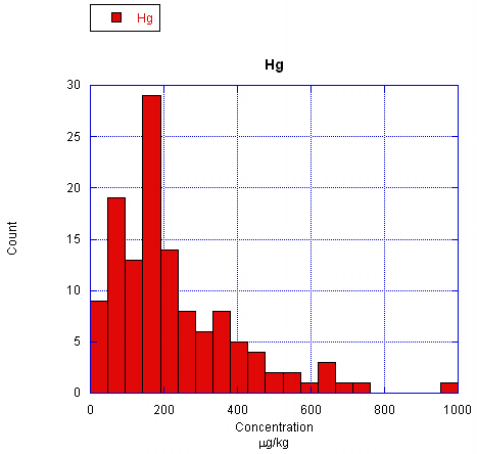
Mercury found in foodstuff has not a natural origin: it's the result of bio-absorption and bioaccumulation through the food chain. The organisms that absorb the greatest amount of Hg from surface waters are fishes. The Hg compound they absorb is the methyl mercury which forms in acidic surface waters. Humans can also uptake mercury from vegetables and other crops on which sprays containing mercury have been applied.

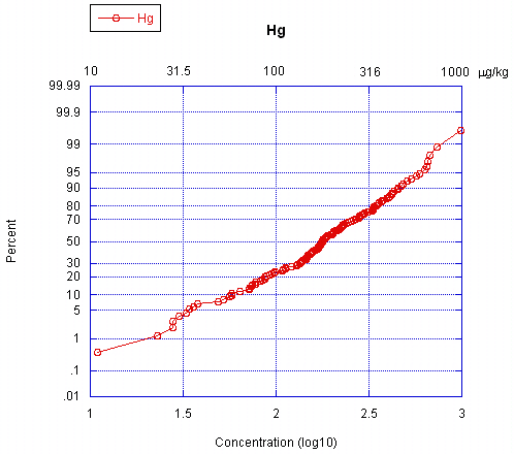
Mercury vapors can be the cause of many health problems, such as nerve, brain and kidney damage, lung irritation, eye irritation and vomiting. Other damages caused by Hg are DNA and chromosomal alteration and reproduction problems such as birth defects and miscarriages.

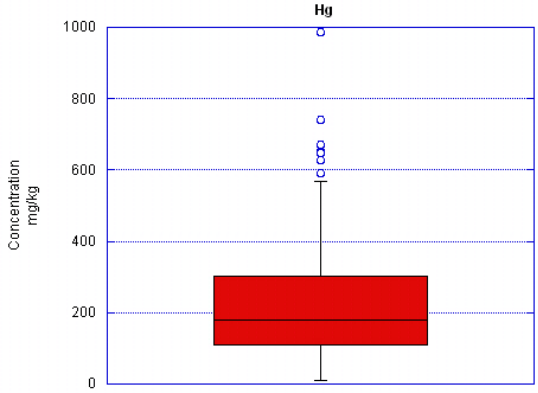
Distribution of Hg concentrationts

Hg higher values (0.57-0.98 mg/kg) are located in the high urbanized areas and near Capodichino international airport. The Hg baseline value distribution shows a trend where the highest Hg baseline values (0.23–0.30 mg/kg) exactly coincide with the mostly urbanized and industrialized areas. The soils of the suburban areas are characterized by baseline values in the range 0.05–0.23 mg/kg, which is identified as natural background values (Cicchella et al. 2005).

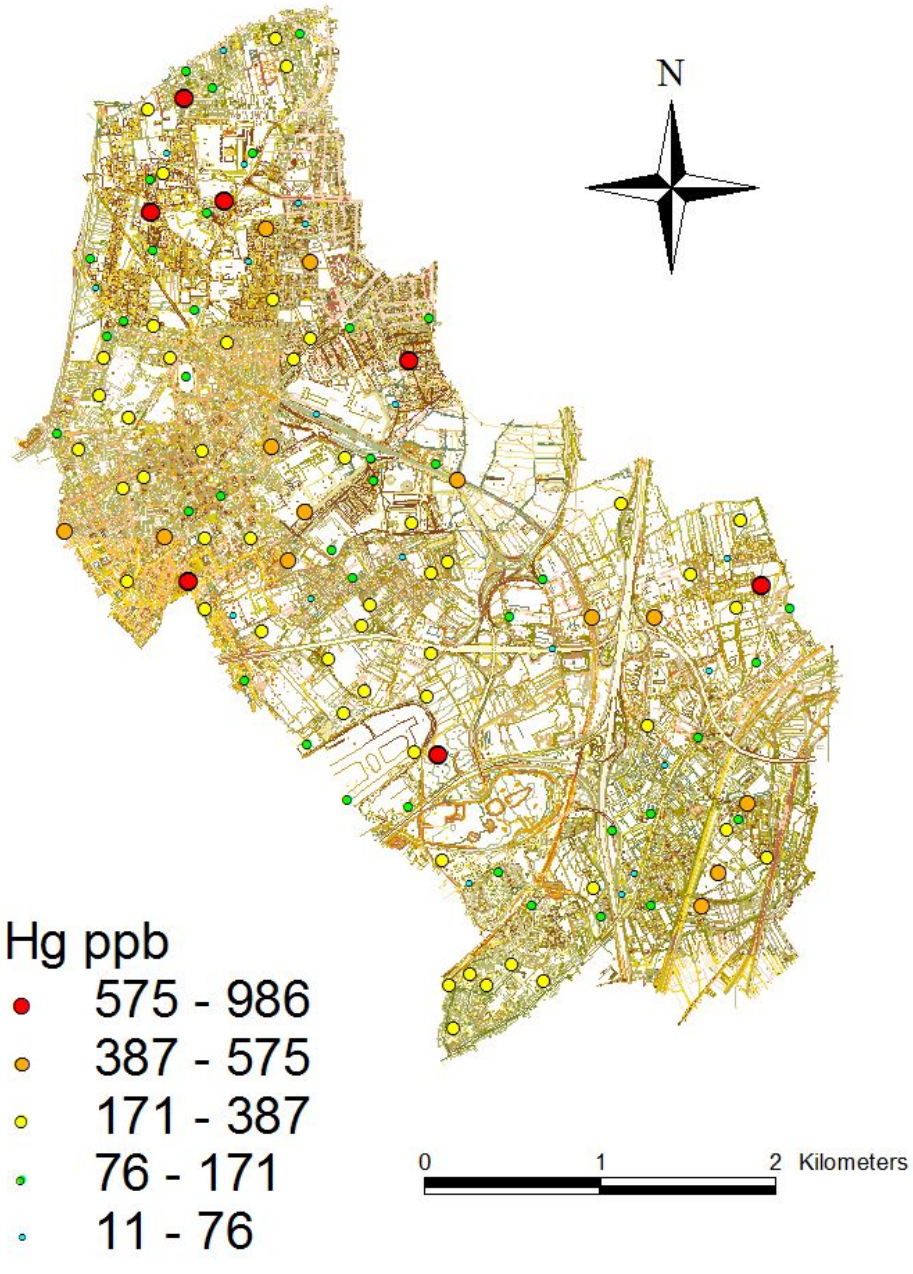
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (1 mg/kg) and industrial soils (5 mg/kg). Casoria soils Hg concentration is lower than D.Lgs.152/06.

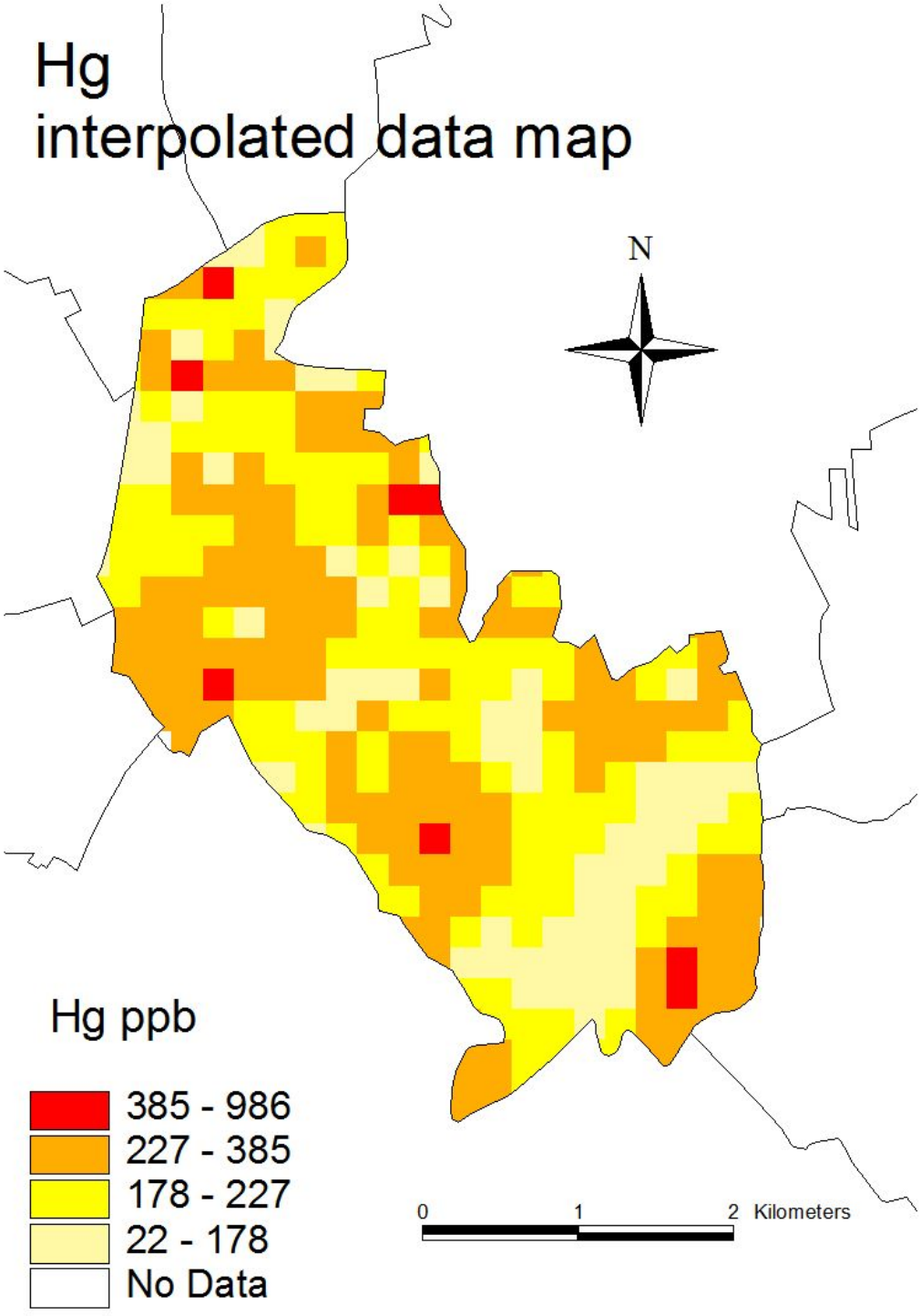

Hg
Hg
Count
Concentration
µg/kg

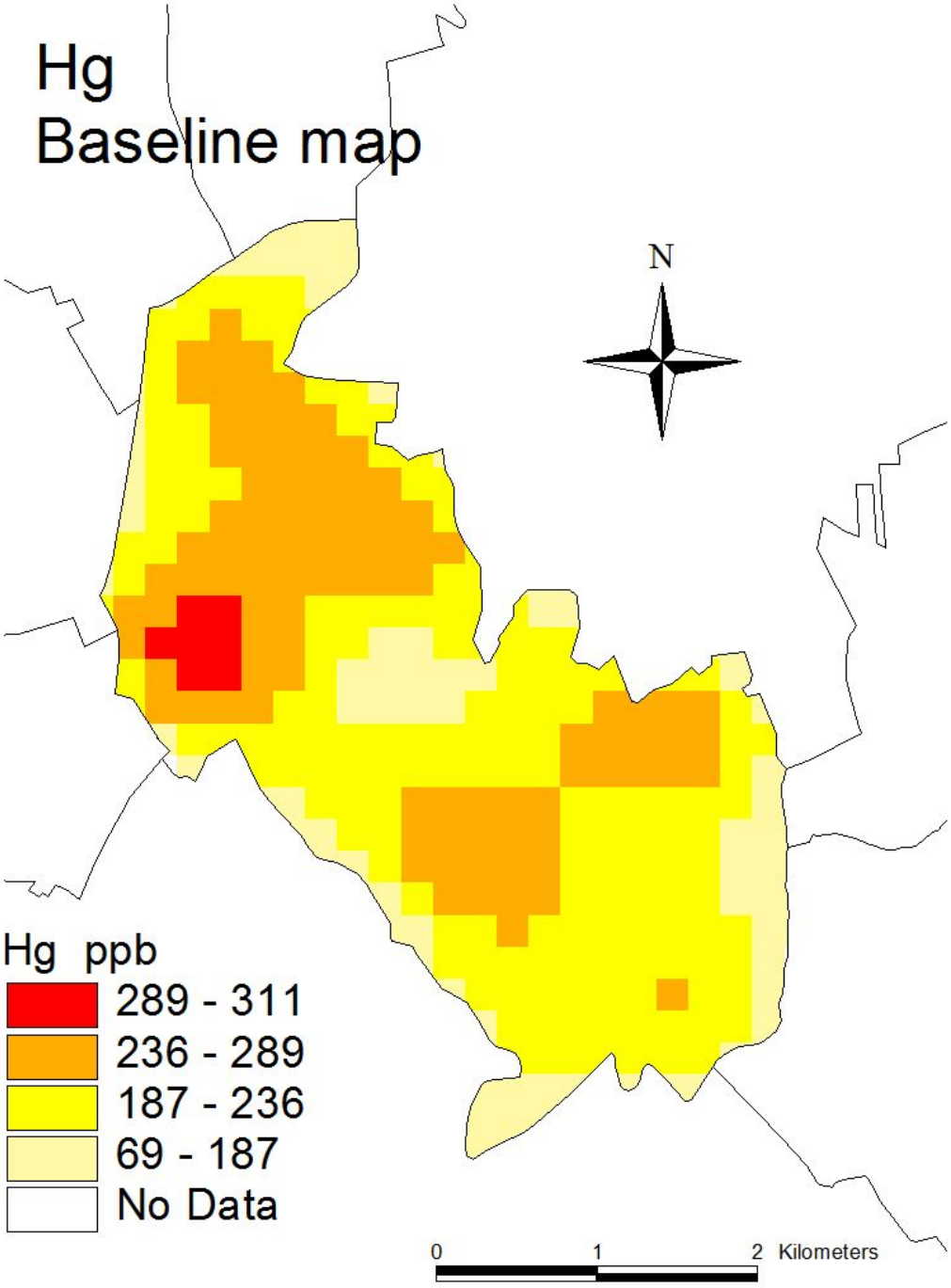

Hg
Hg
Percent
Concentration (log10)
µg/kg


Hg
Concentration
mg/kg

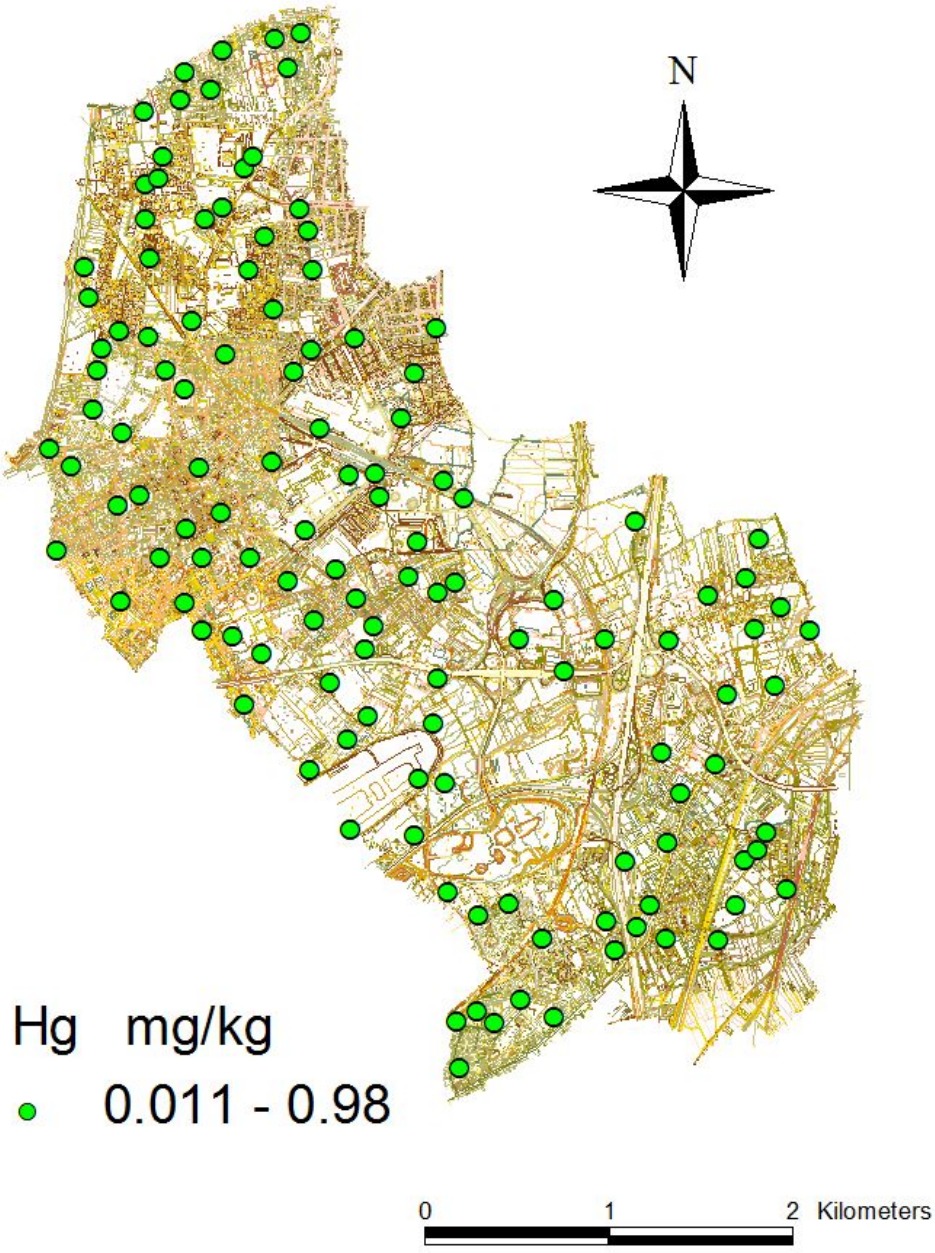
Hg
Dot Map




Hg
interpolated data map
N
Hg ppb
385 - 986
227 - 385
178 - 227
22 - 178
No Data
0
1
2 Kilometers


Hg
Baseline map
N
Hg ppb
289 - 311
236 - 289
187 - 236
69 - 187
No Data
0
1
2 Kilometers

Hg
Risk map (D.Lgs. 152/06)
Residential threshold 1 mg/kg



Nickel (Ni)

Nickel is a ductile metal, it is a fairly good conductor of heat and electricity.

It is mainly employed for the production of many ductile, strong, heat and corrosion resistant alloys. Nickel is also used in rechargeable batteries, catalysts, coinage, foundry products, plating and jewelry.

Nickel mostly occurs combined with sulphur and arsenic; it is mainly extracted in ironnickel sulphides ores and its major mining districts are Russia, Australia, New Caledonia, Cuba, Canada and South Africa.

The average nickel content in soils is around 20 ppm, but it can vary between 0.2 ppm and 450 ppm. Foodstuffs naturally contain small amounts of nickel; its major food sources are beans and tea; also chocolate and fats are known to contain high Ni contents.

Nickel can enter human body through breathing, smoking cigarettes, and drinking or eating food containing high Ni values, but also through skin contact with nickel contaminated soils or waters.

If assumed in small quantities nickel is an essential element, too high concentrations can be a harm to human health and cause problems such as: skin rashes and allergic reactions, lung embolism, asthma and chronic bronchitis, heart problems and higher chances of cancer development.

Anthropic activities releasing Ni into the air, are power plants and trash incinerators; it is also released in surface water when it's contained in wastewater streams.

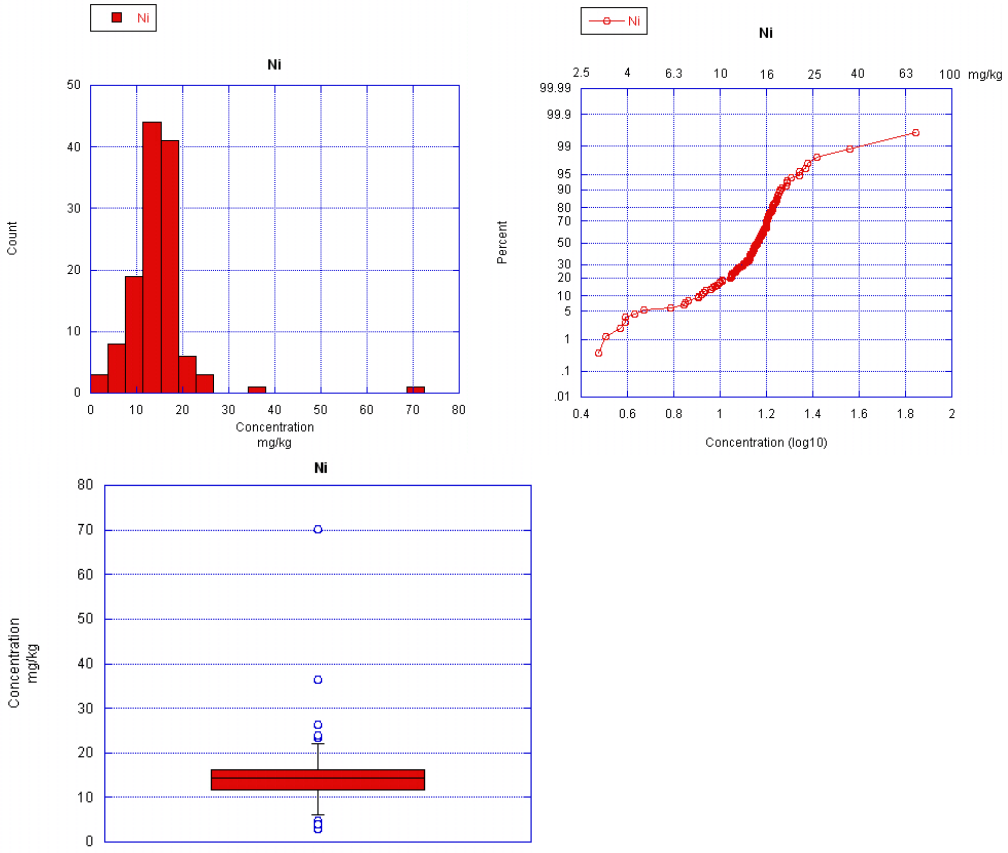
For animals small amounts of nickel are an essential nutrient, but uptake in excessive doses can also be dangerous. Nickel doesn't accumulate in plants or animals so it doesn't bio magnify up the food chain.

Distribution of Ni concentrationts

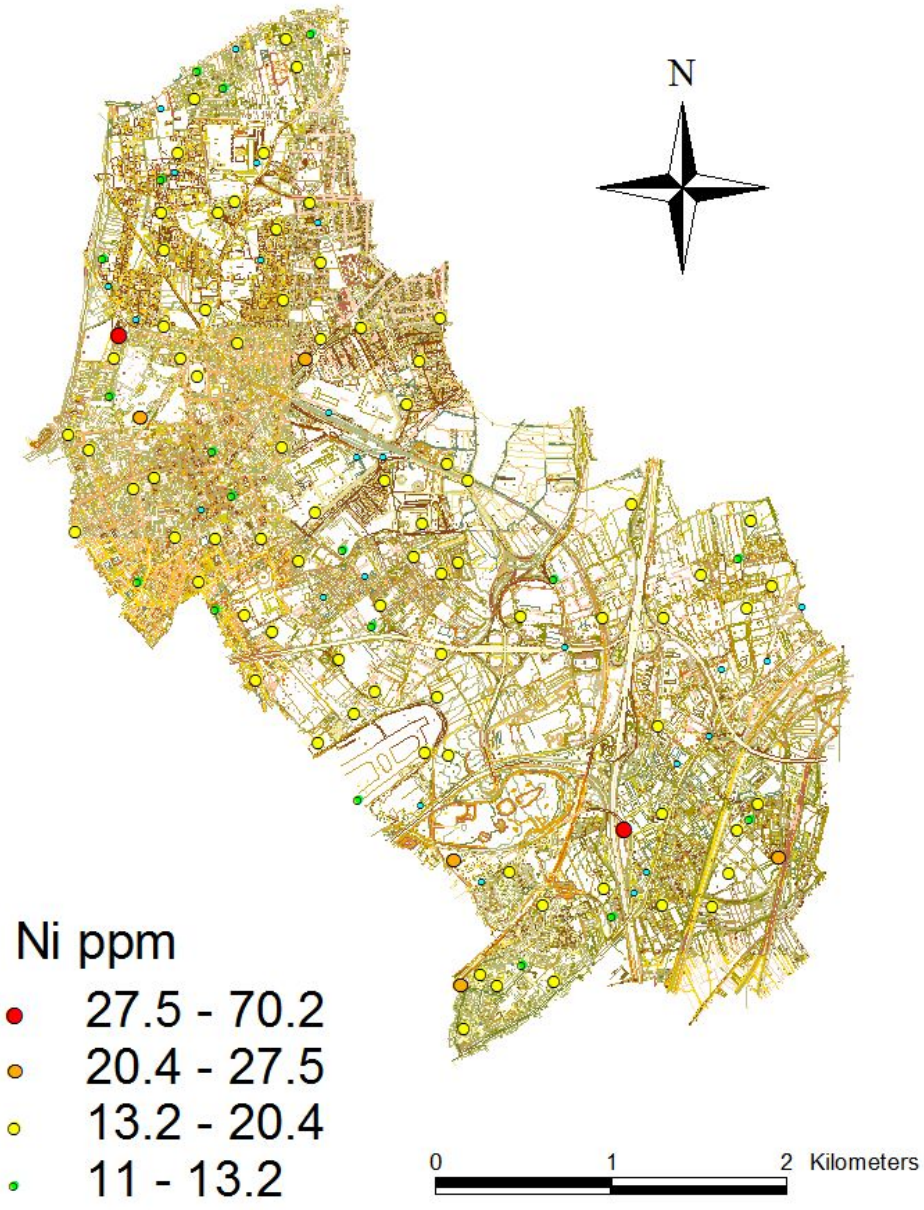
Nickel concentration misured in Casoria soils shows in almost all studied area low value (3 – 27 mg/kg) clearly consistent with baseline values, only 2 samples shows high concentration (27 – 70 mg/kg).

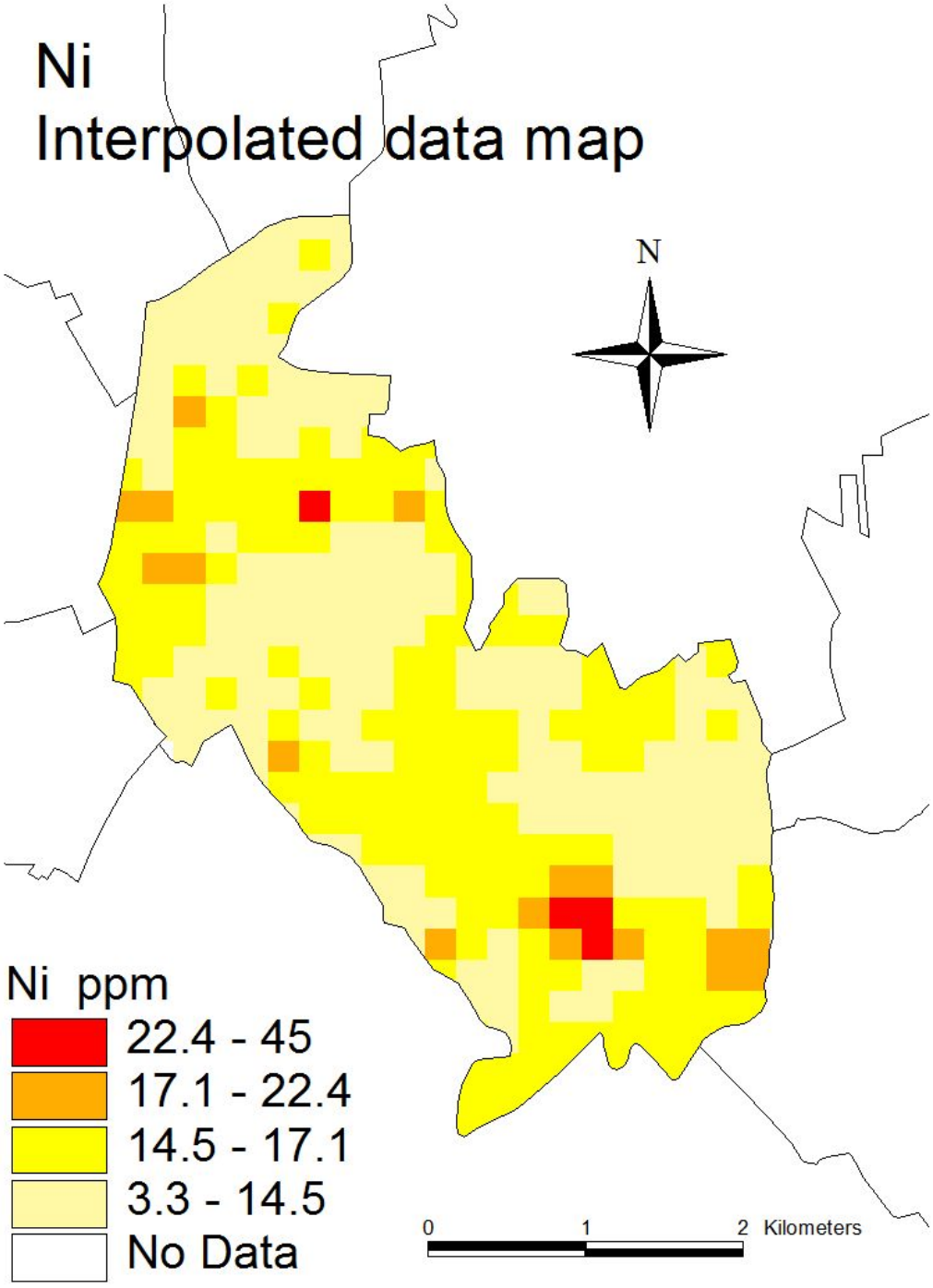
The average Ni content in soils is 15 mg/kg which is considered Caasoria natural background, so values up 15 mg/kg are anthropically influenced, is possible to link anthropic influence with north-western urbanized areas and in the southern sector Arpino urbanizaed area.

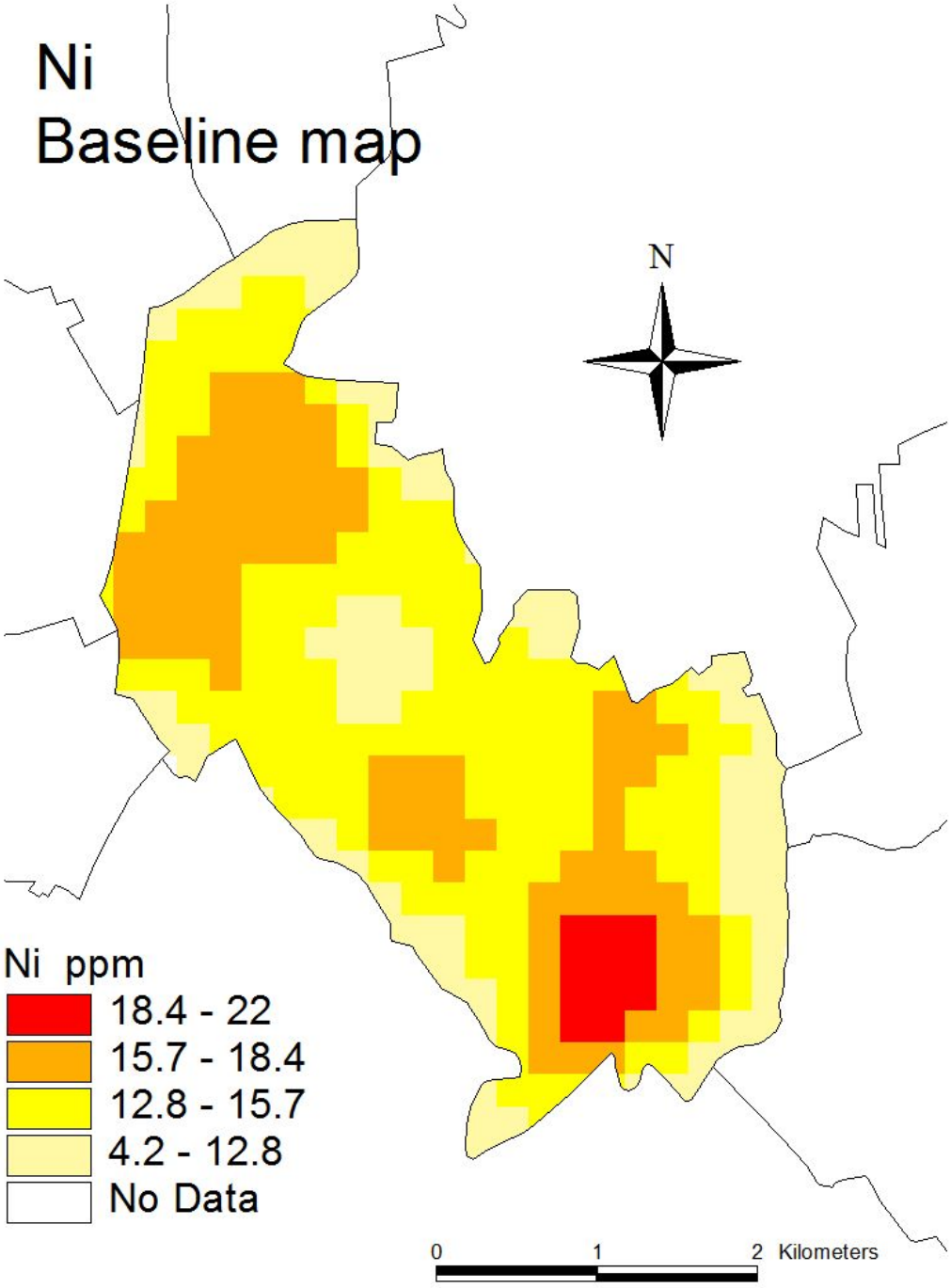
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (120 mg/kg) and industrial soils (500 mg/kg). Casoria soils Ni concentration is lower than D.Lgs.152/06.


Ni
Ni
Count
Concentration
mg/kg
Ni
Percent
Concentration (log10)
mg/kg
Ni
Concentration
mg/kg

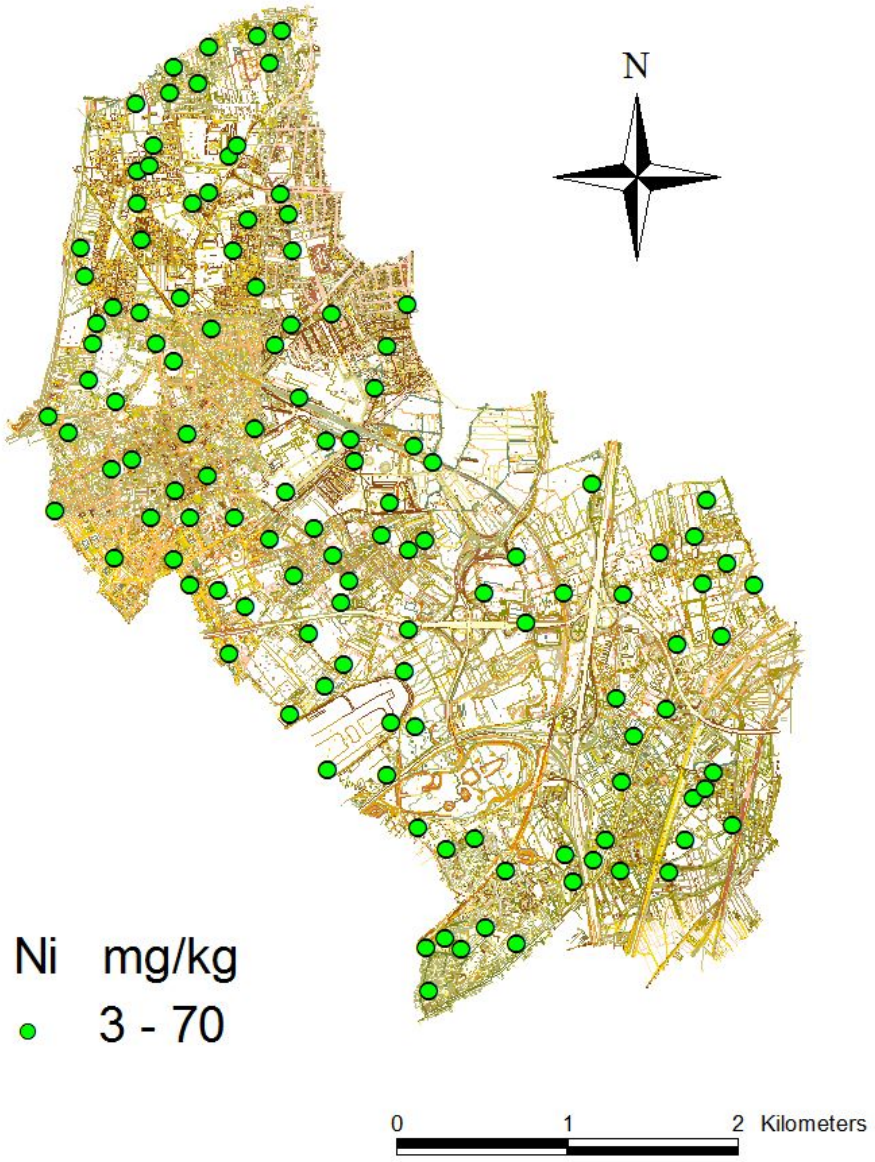
Ni
Dot Map




Ni
Interpolated data map
N
Ni ppm
22.4 - 45
17.1 - 22.4
14.5 - 17.1
3.3 - 14.5
No Data
0
1
2 Kilometers


Ni
Baseline map
N
Ni ppm
18.4 - 22
15.7 - 18.4
12.8 - 15.7
4.2 - 12.8
No Data
0
1
2 Kilometers

Ni
Risk map (D.Lgs. 152/06)
Residential threshold 120 mg/kg



Lead (Pb)

Lead is a metal element, with a relatively poor electricity conductivity and a high resistance to corrosion. Its isotopes are the end products of each of the three series of naturally occurring radioactive elements.

One of the main applications of Pb is for the production of lead-acid car batteries; it's also used in ceramic glazes, in organ pipes, as electrodes and in computers and televisions screens with the function of radiations shield for viewers.

The main lead mineral is Galena (PbS), it's mined in Australia, USA, China, Peru' and Canada. Some lead is also mined in Mexico and Germany.

Even if lead is a naturally occurring element, most of its environmental concentrations are the result of anthropic activities, especially of leaded gasoline combustion and of industrial emissions and waste disposals.

The lead-cycle created by human activities is much more extended than the natural leadcycle, this has caused lead pollution to be a worldwide problem. Lead can be added to human body through contaminated food, water and air; it is one of metals with the most harmful effects on human health. It can cause: disruption of the biosynthesis of hemoglobin and anemia, rise in blood pressure, kidney damage, miscarriages and subtle abortions, brain damage and many others.

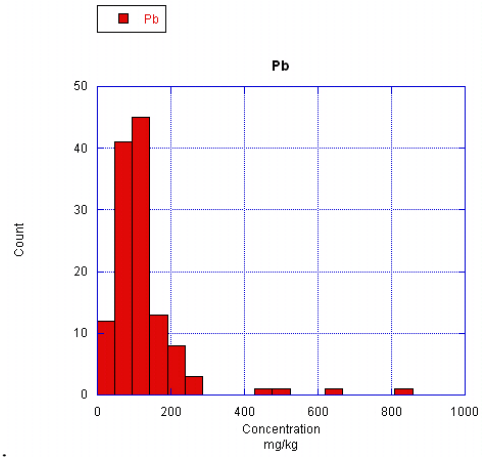
During pregnancy lead can enter into the fetus through mother placenta and can cause serious damages to the nervous system and the brains of unborn children.

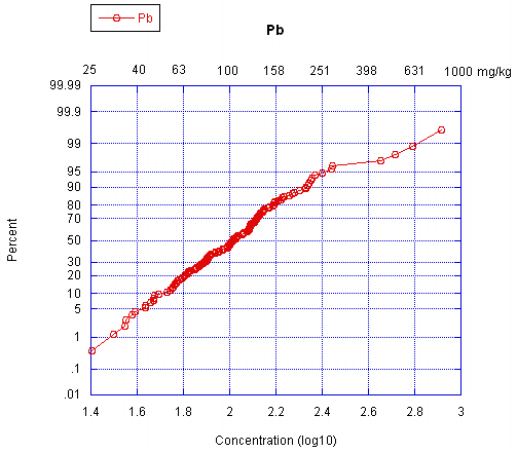
Distribution of Pb concentrationts

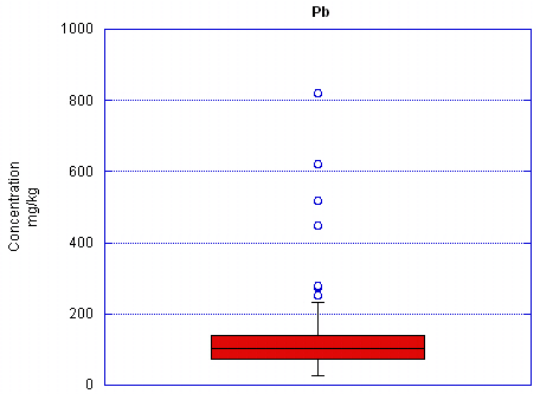
Lead highest value (185-821 mg/kg) has been detected in the western area of Comune di Casoria, on the Naples border. The lead baseline value distribution shows the highest values (100–312 mg/kg) in most of municipal territory that might reflect how anthropogenic contribution overlap geogenic one.

Soils collected in the nord east suburban fields, not anthropogenically influenced, show concentration values in the range 35–83 mg/kg, which is assumed as the natural background values (Cicchella et al. 2005).

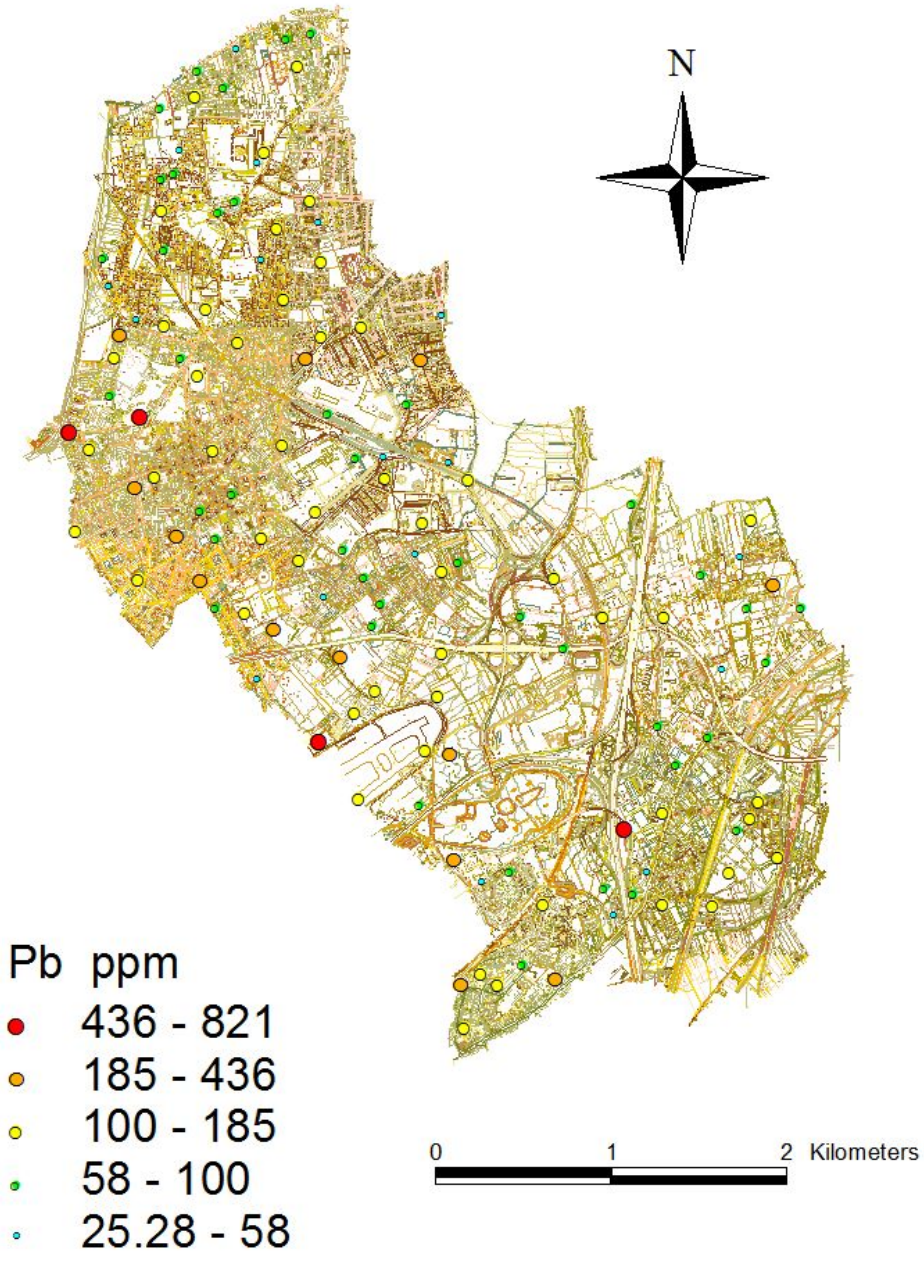
Environmental Italian Law (D.Lgs. 152/06) fix concentration limit for residential soils (100 mg/kg) and industrial soils (1000 mg/kg). Casoria soils shows higher values than D.Lgs. 152/06 in several areas principally in the western sector on the City of Naples border.

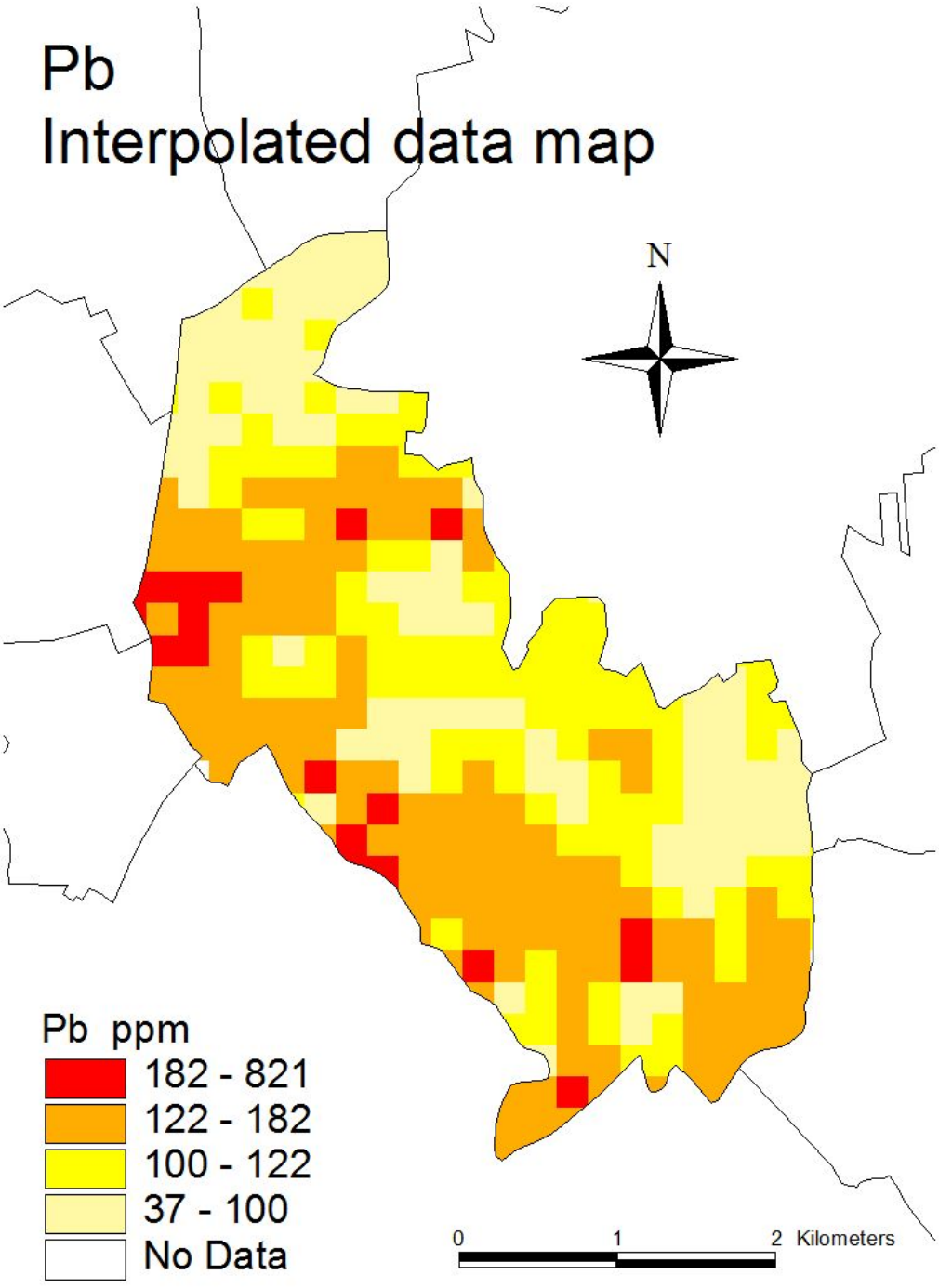

Pb
Pb
Count
Concentration
mg/kg
0
10
20
30
40
50
0
200
400
600
800
1000

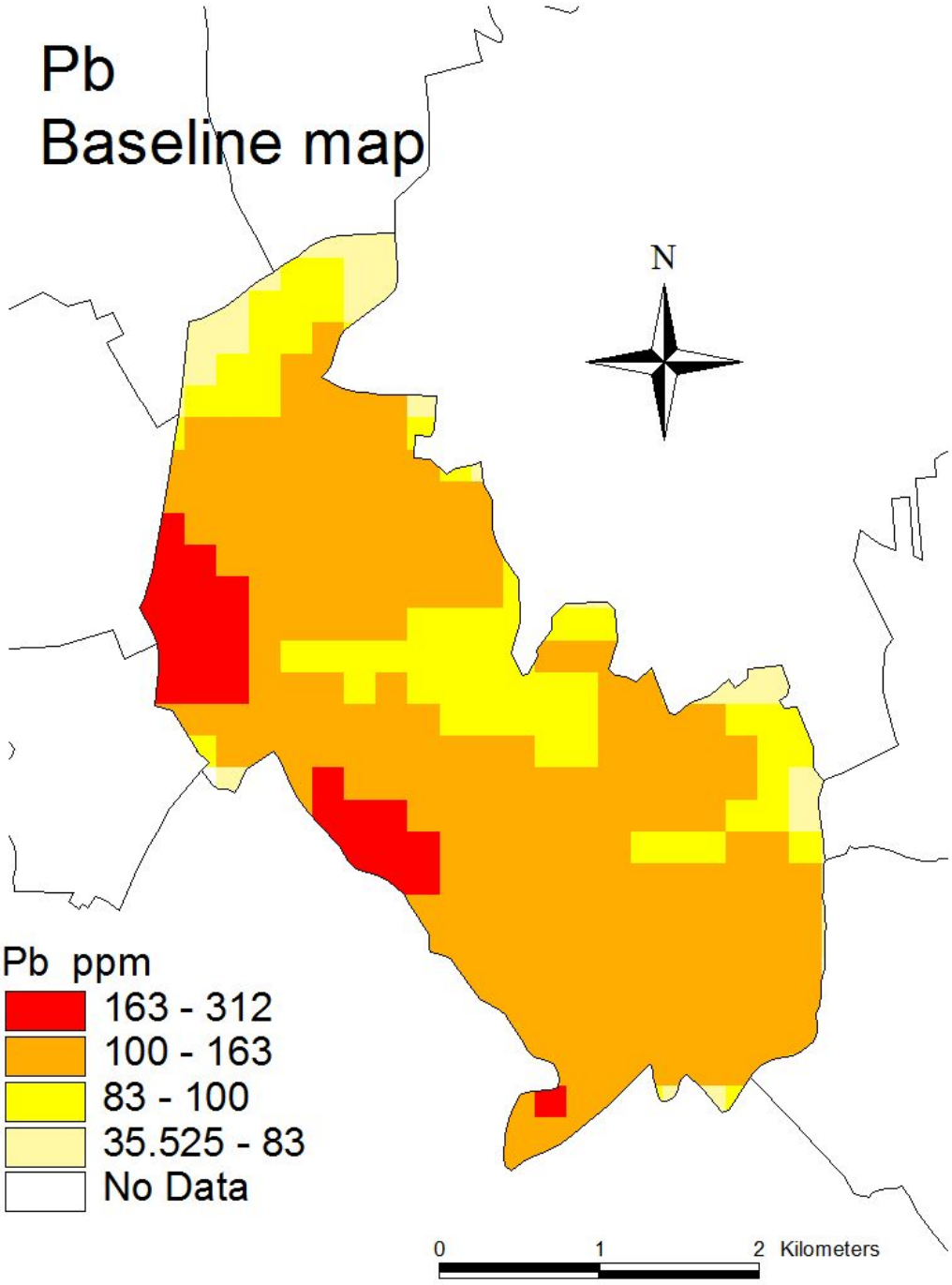

Pb
Pb
Percent
Concentration (log10)
25
40
63
100
158
251
398
631
1000 mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3


Pb
Concentration
mg/kg
0
200
400
600
800
1000

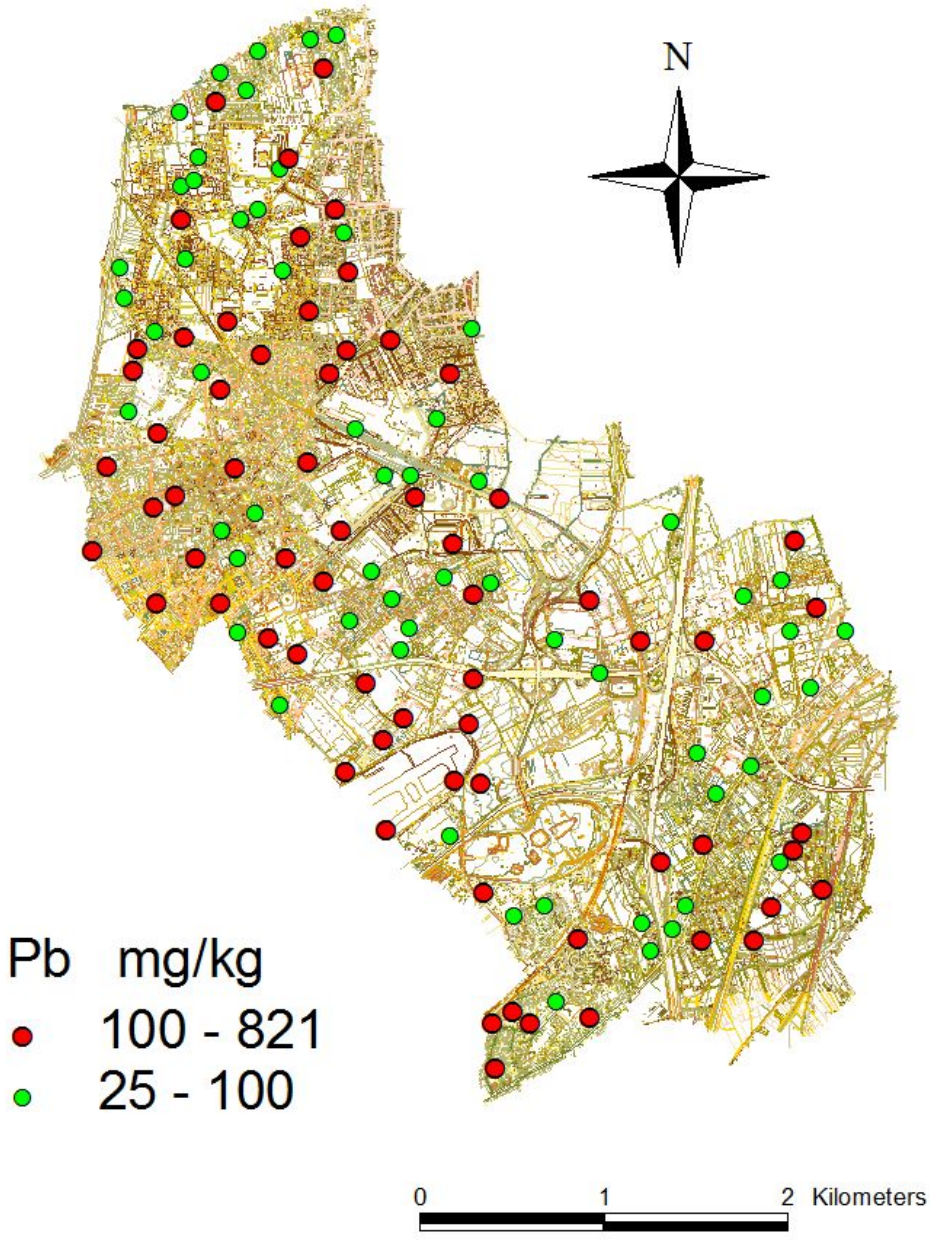
Pb
Dot Map




Pb
Interpolated data map
N
Pb ppm
182 - 821
122 - 182
100 - 122
37 - 100
No Data
0
1
2 Kilometers


Pb
Baseline map
N
Pb ppm
163 - 312
100 - 163
83 - 100
35.525 - 83
No Data
0
1
2 Kilometers

Pb
Risk map (D.Lgs. 152/06)
Residential threshold 100 mg/kg



Antimony (Sb)

Antimony is a semimetallic element with a low conductivity of heat and electricity.

Its compounds are used in paints, ceramics and pottery; its alloys are used in batteries while pure antimony is used to make diodes and infrared detectors.

Sometimes it's found free in nature, but is usually obtained from the ores stibnite (Sb2S3) and valentinite (Sb2O3). Antimony is an important economic metal and its main production countries are Russia, China, Bolivia and South Africa.

Antimony in the environment can be the result of both naturally occurring contents and

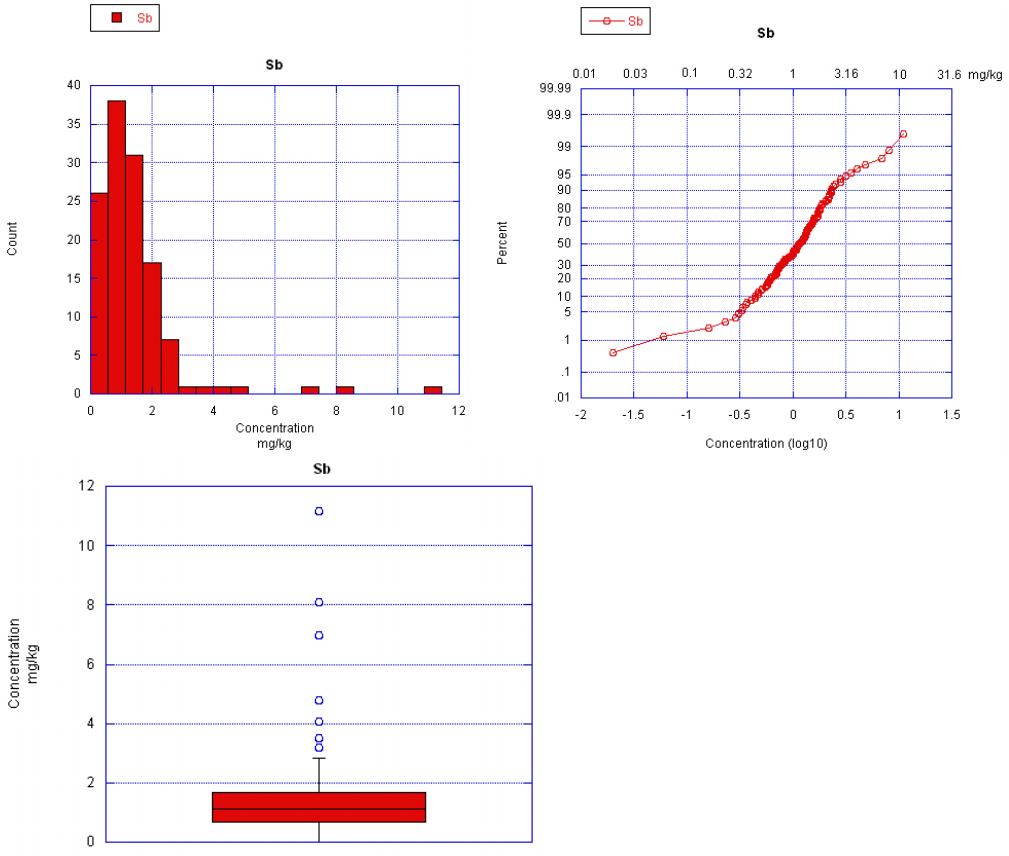
several human activities. The main human exposure ways to Sb are breathing in its dusts, drinking waters and eating foods, but also skin contact with soils and waters containing it. Prolonged high Sb concentrations exposure can cause irritation of the eyes, skin and lungs. As the exposure continues more serious health effects may occur, such as lung diseases, heart problems, diarrhea, severe vomiting and stomach ulcers.

Distribution of Sb concentrationts

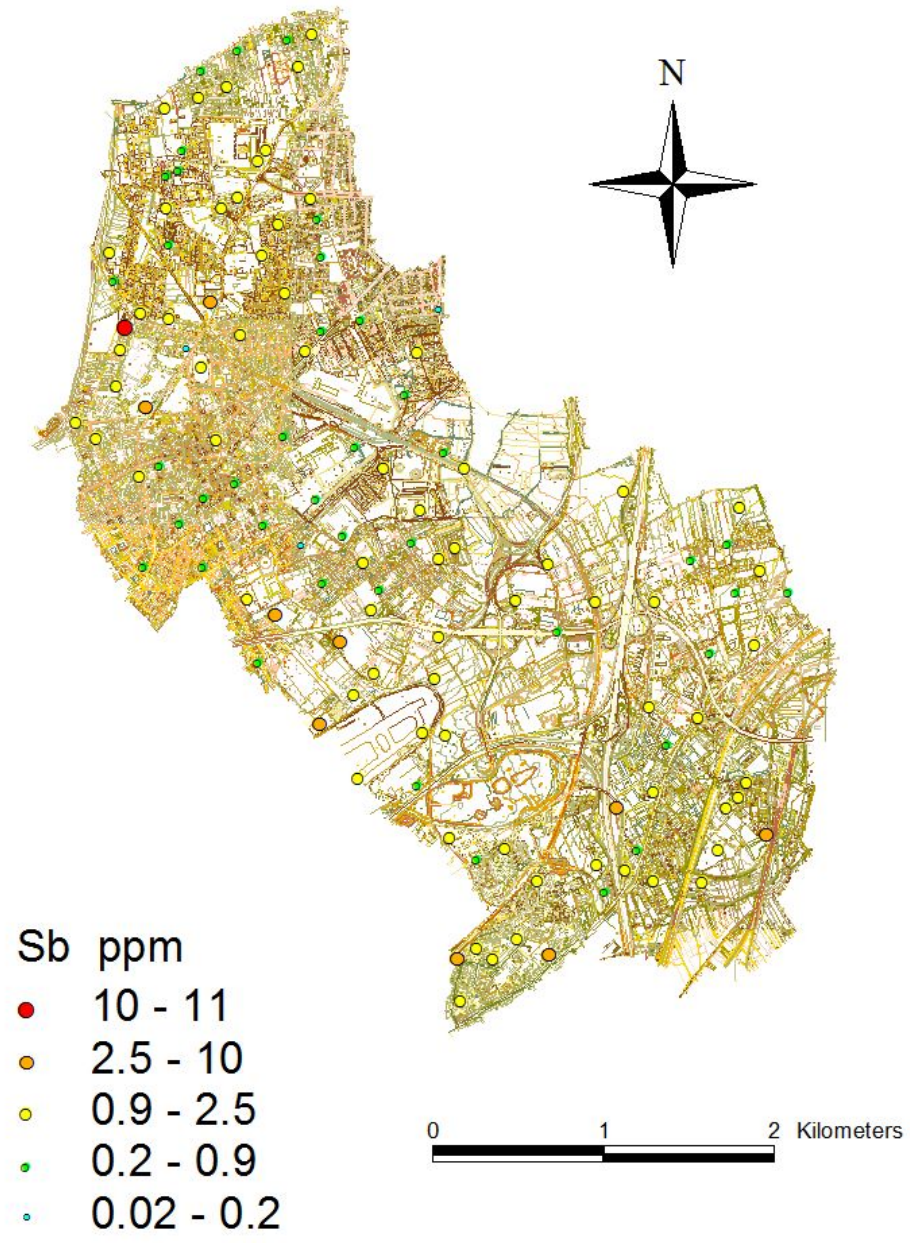
Antimony baseline value distribution shows the highest values (from 1.4 to 2.7 mg/kg) in the northern and southern areas of Comune di Casoria corresponding to the higher urbanized areas and might reflect both geogenic and anthropogenic contribution.

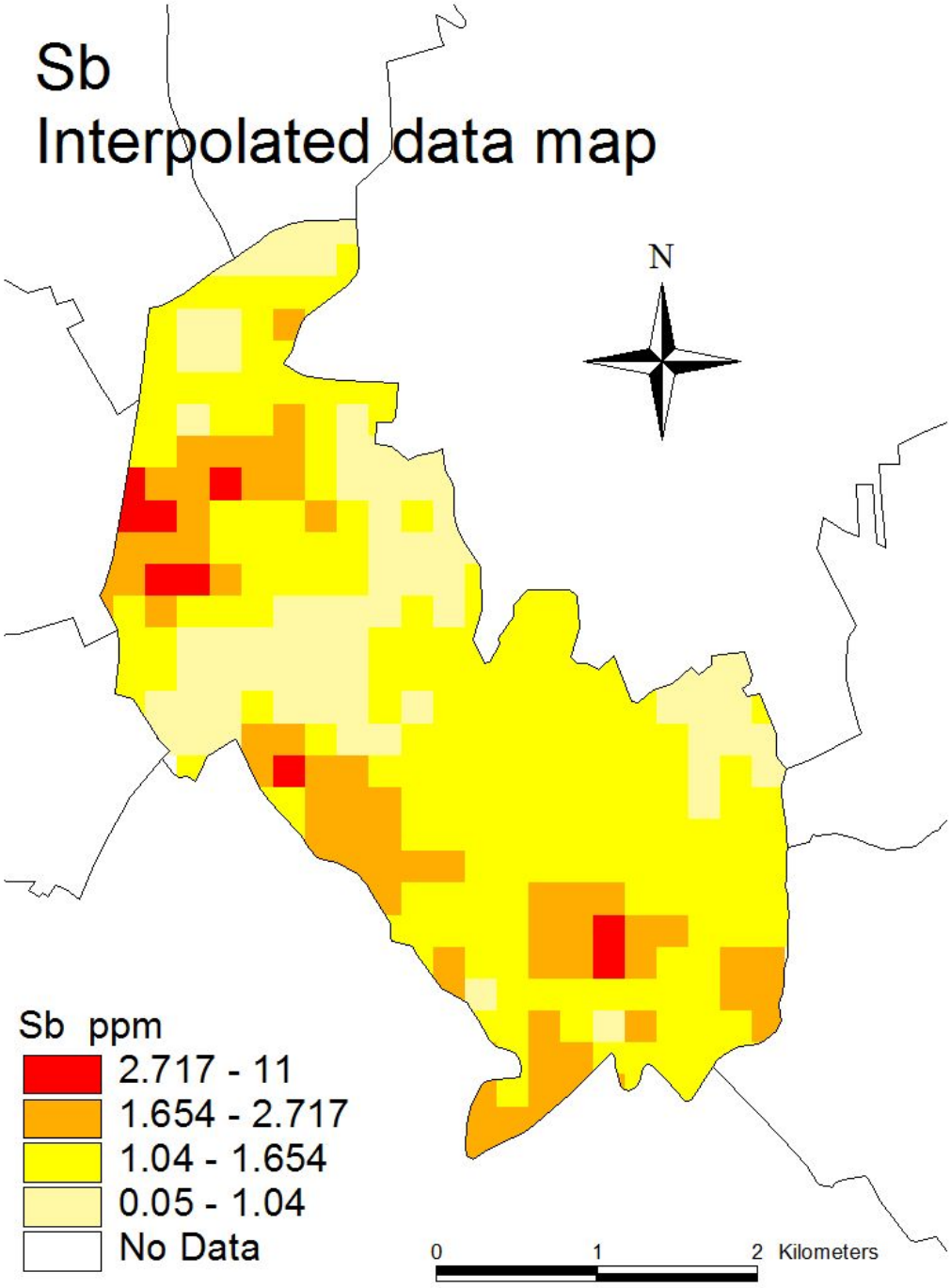
Suburban and rural areas show concentration values in the range 0.1 to 1.4 mg/kg, which is considered the natural background values (Cicchella et al. 2005).

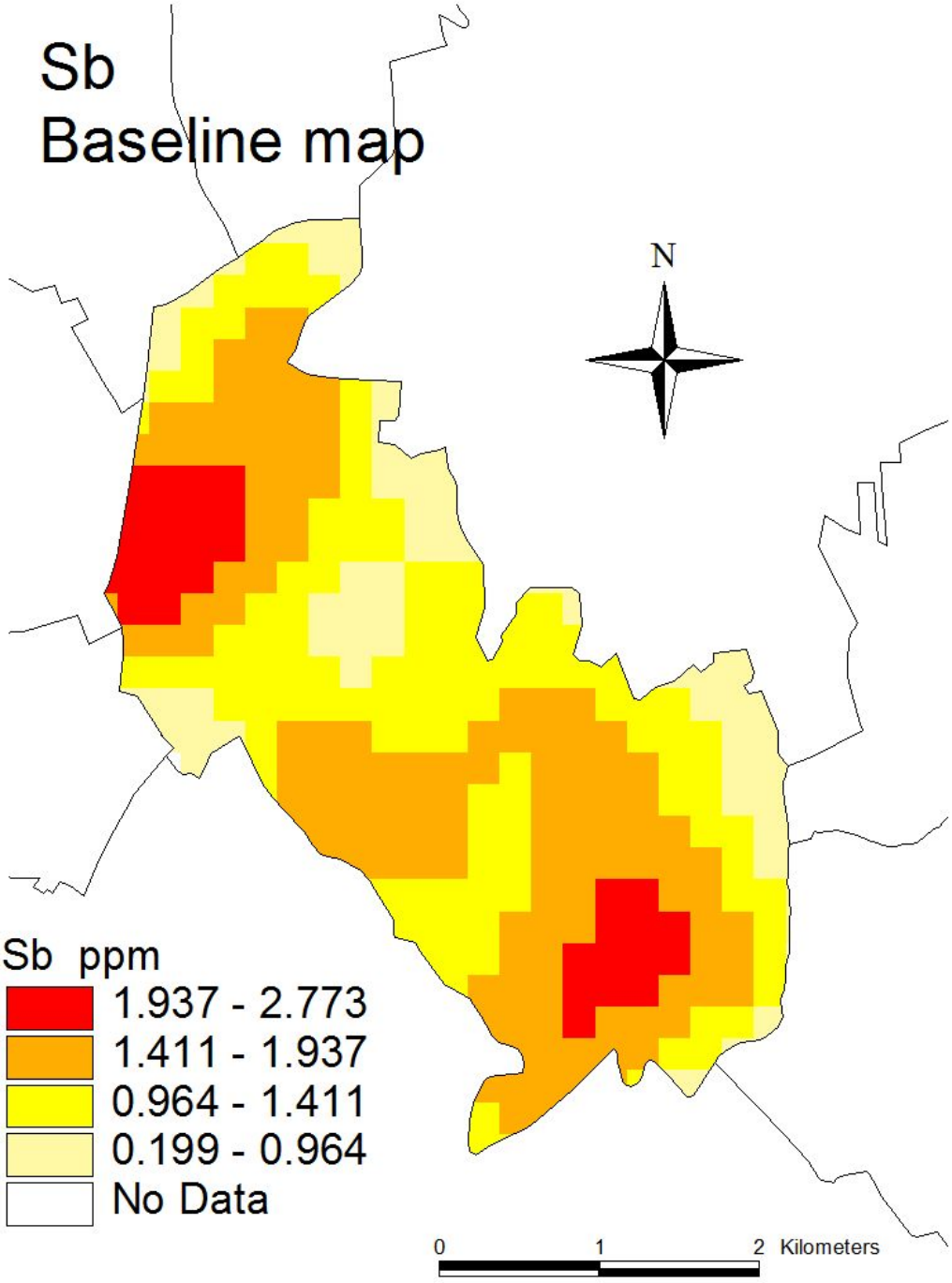
Compared to Naples in which the high baseline values (3–6 mg/kg) have clearly an anthropogenic origin due to motor vehicle traffic, Casoria soils showes the same trend, whit the highest values (2.5-11 mg/kg) in the urban areas on the border with Naples.



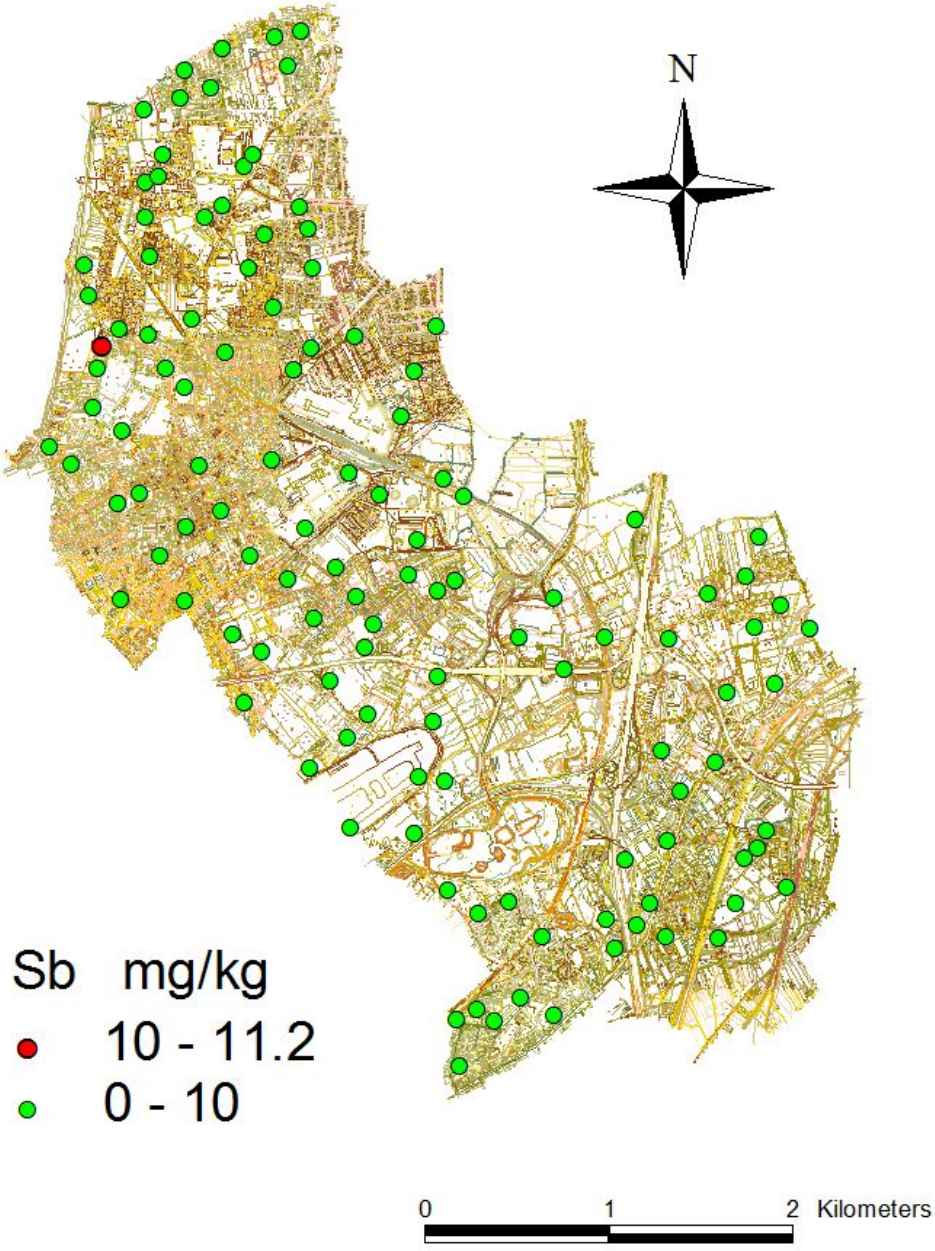
Sb
Dot Map




Sb
Interpolated data map
N
Sb ppm
2.717 - 11
1.654 - 2.717
1.04 - 1.654
0.05 - 1.04
No Data
0
1
2 Kilometers


Sb
Baseline map
N
Sb ppm
1.937 - 2.773
1.411 - 1.937
0.964 - 1.411
0.199 - 0.964
No Data
0
1
2 Kilometers

Sb
Risk map (D.Lgs. 152/06)
Residential threshold 10 mg/kg



Selenium (Se)

Selenium is a non metallic element. The crystalline metal allotropic form, also known as metallic selenium, has a higher electrical conductivity in the light than in the dark, and is used in photocells.

Due to its good photovoltaic and photoconductive properties, it's widely used in electronics; other uses of selenium are in the glass industry, in rubbers vulcanization, for animal feeds and food supplements production, in photography and in metal alloys as the one used in rectifiers of AC-DC current.

The main selenium producing countries are Canada, USA, Bolivia and Russia.

Selenium can be released into the environment through both natural processes and human activities.

Agricultural soils on which phosphate fertilizers have been used, usually have high Se contents. The reaction of selenium with oxygen cause the element to be mobile and dissolve into water. Therefore in soils with high acidity, selenium is mobilized and, the chances of exposure to its compounds increase, becoming a threat for human health. High soils acidity is usually the result of human activities such as industrial and agricultural processes. Other parameters influencing selenium mobilization and its velocity are temperatures, moisture, organic matter content and microbial activity.

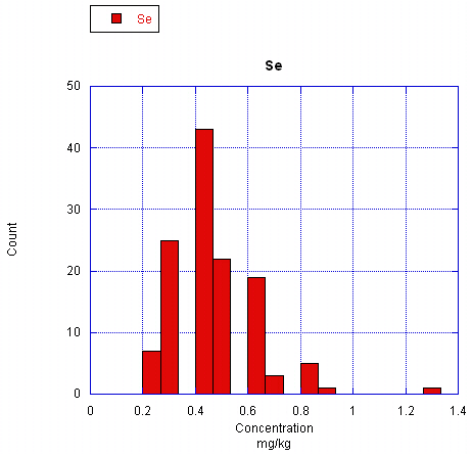
Human exposure to selenium can occur through food or water, or through contact with soil or air containing high concentrations of selenium. In foodstuffs such as grains, cereals and meat, selenium is naturally present.

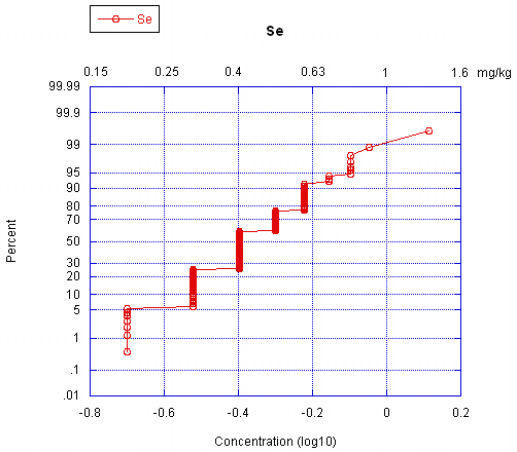
It is an element necessary for humans in order to maintain good health. By the way, high and prolonged selenium exposure can cause the collection of fluid in the lungs and lead to bronchitis, but also chills, fever, headache, conjunctivitis, vomiting, abdominal pain and enlarged liver. Selenium shortages can cause heart and muscle problems. In some cases selenium poisoning may even lead to death.

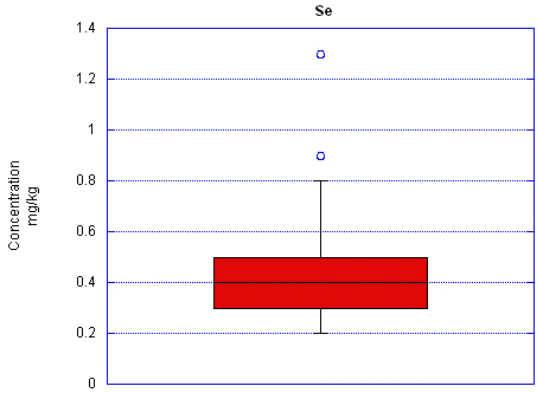
Selenium can accumulate in the body tissues of organisms and can then be passed up through the biological cycle. Selenium contents tend to be very high in aquatic organisms in many areas because of the irrigation run-off from fertilized soils.

Distribution of Se concentrationts

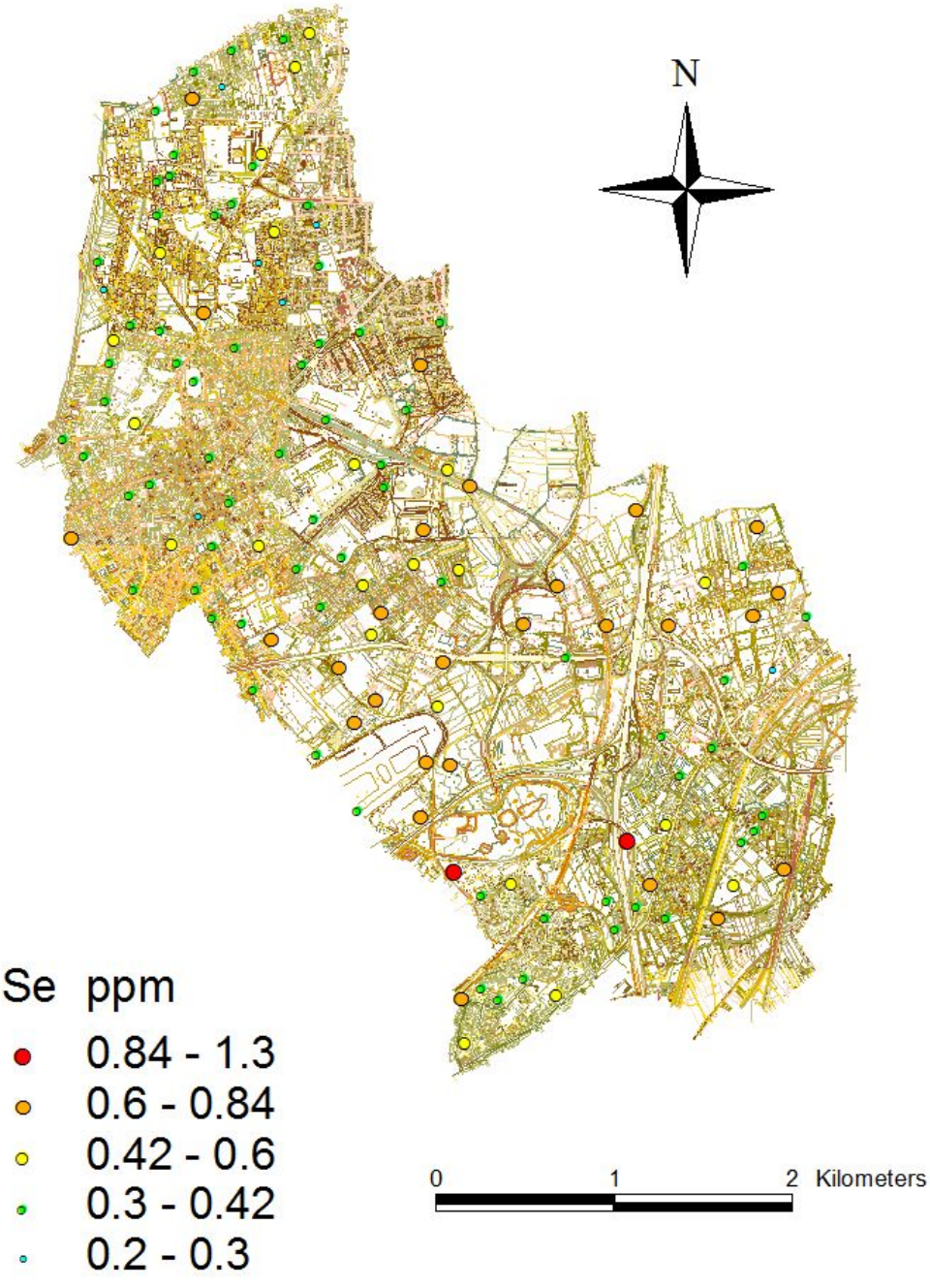
The soils of the whole Casoria territory are characterized by Se baseline values in the range 0.1–0.7 mg/kg and the highest value detected is 1.3 mg/kg. which is considered as coincident with natural background values for soils of the entire Neapolitan area (Cicchella et al. 2005).

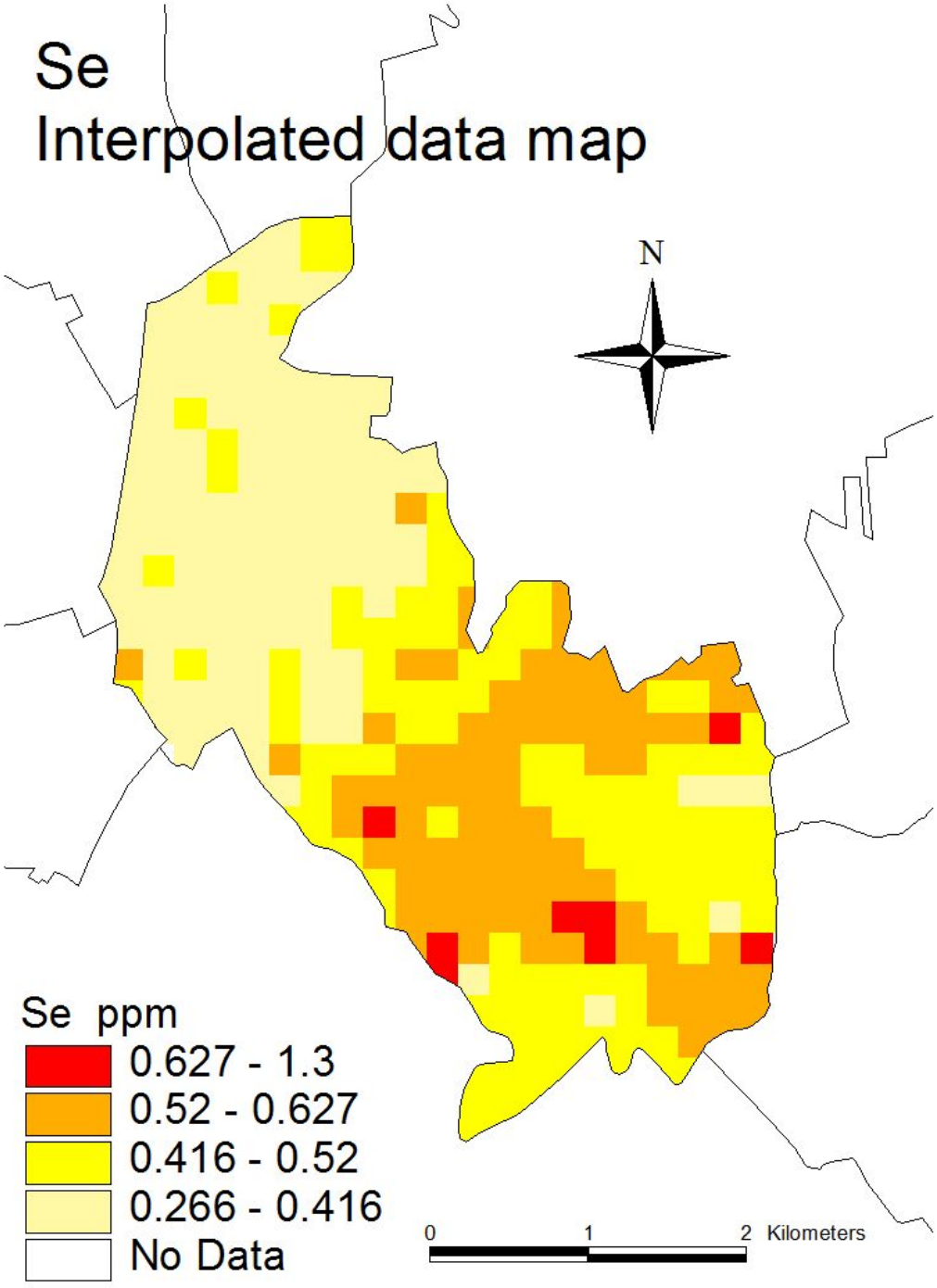

Se
Se
Count
Concentration
mg/kg

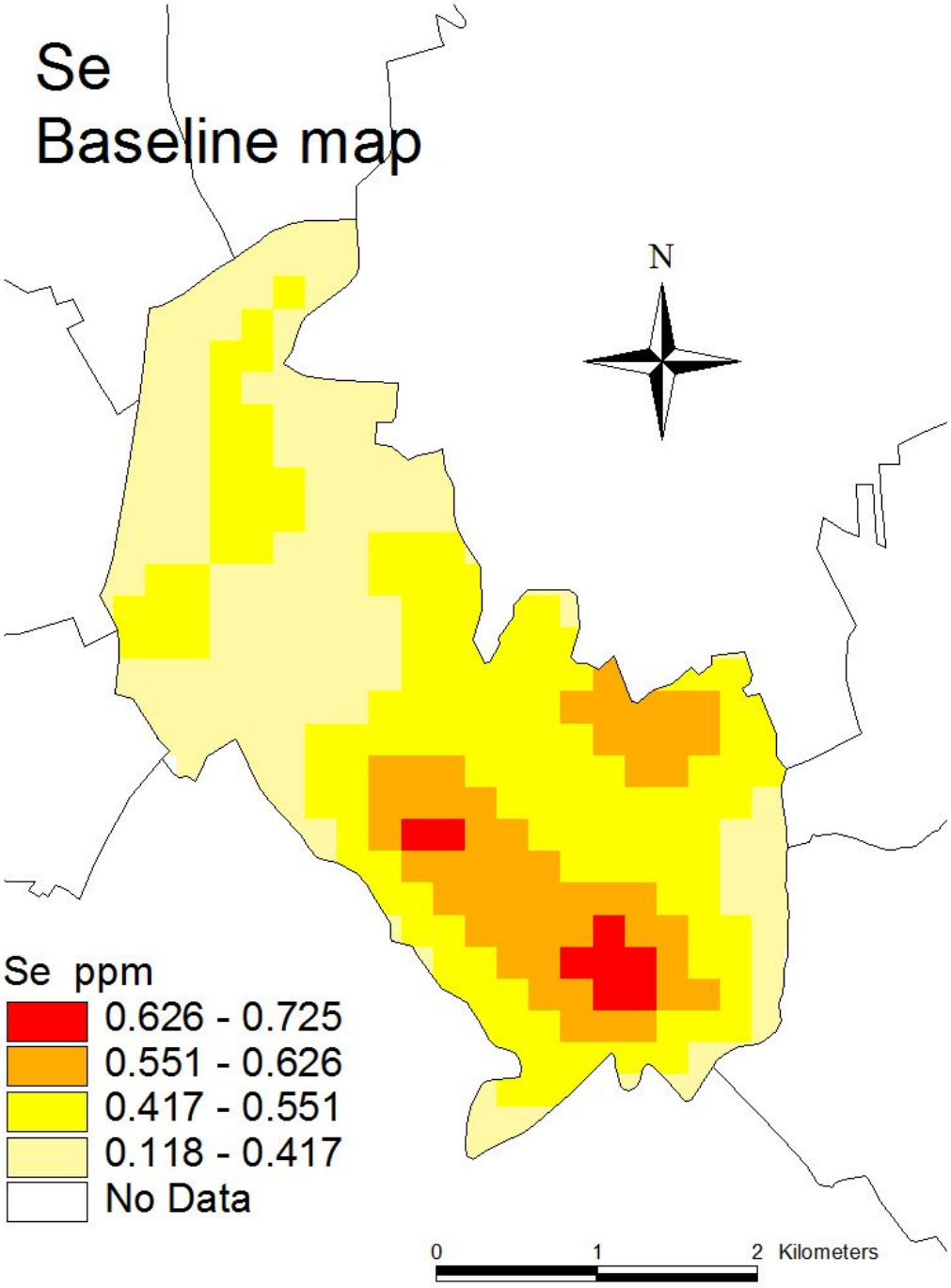

Se
Se
0.15
0.25
0.4
0.63
1
1.6
mg/kg
Percent
Concentration (log10)


Se
Concentration
mg/kg

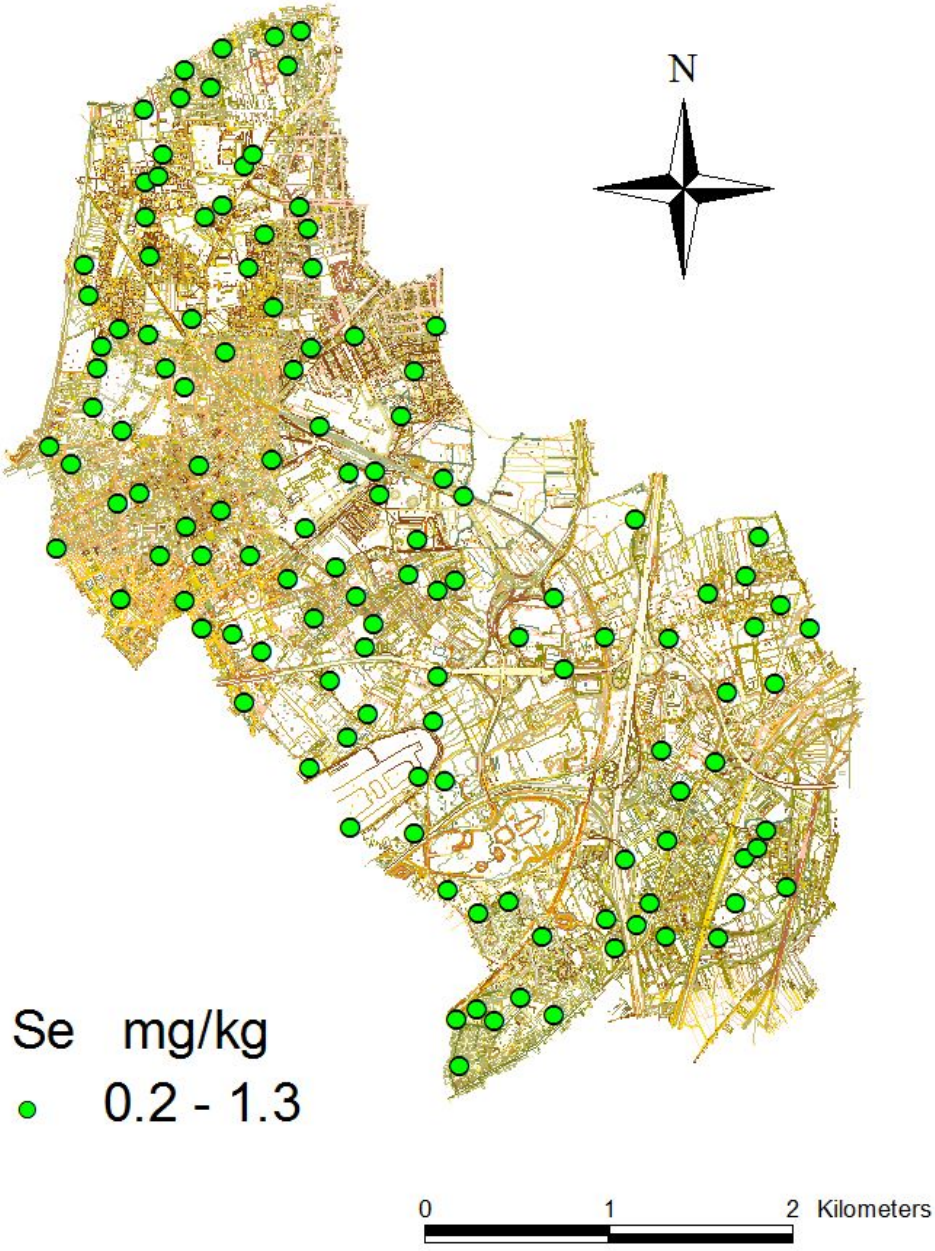
Se
Dot Map




Se
Interpolated data map
N
Se ppm
0.627 - 1.3
0.52 - 0.627
0.416 - 0.52
0.266 - 0.416
No Data
0
1
2 Kilometers


Se
Baseline map
N
Se ppm
0.626 - 0.725
0.551 - 0.626
0.417 - 0.551
0.118 - 0.417
No Data
0
1
2 Kilometers

Se
Risk map (D.Lgs. 152/06)
Residential threshold 3 mg/kg



Thallium (Tl)

Thallium is a metal very soft and malleable.

Due to its low melting point it's used in special glass production and in thermometers for low temperature. Other uses are: in photocells, for sink-float separation of minerals, as reagent in chemical research, as rat poison and as a pesticide in developing countries (its sulphate is banned in western countries).

Thallium minerals are rare, it is mainly found in potassium minerals such as sylvite and pollucite.

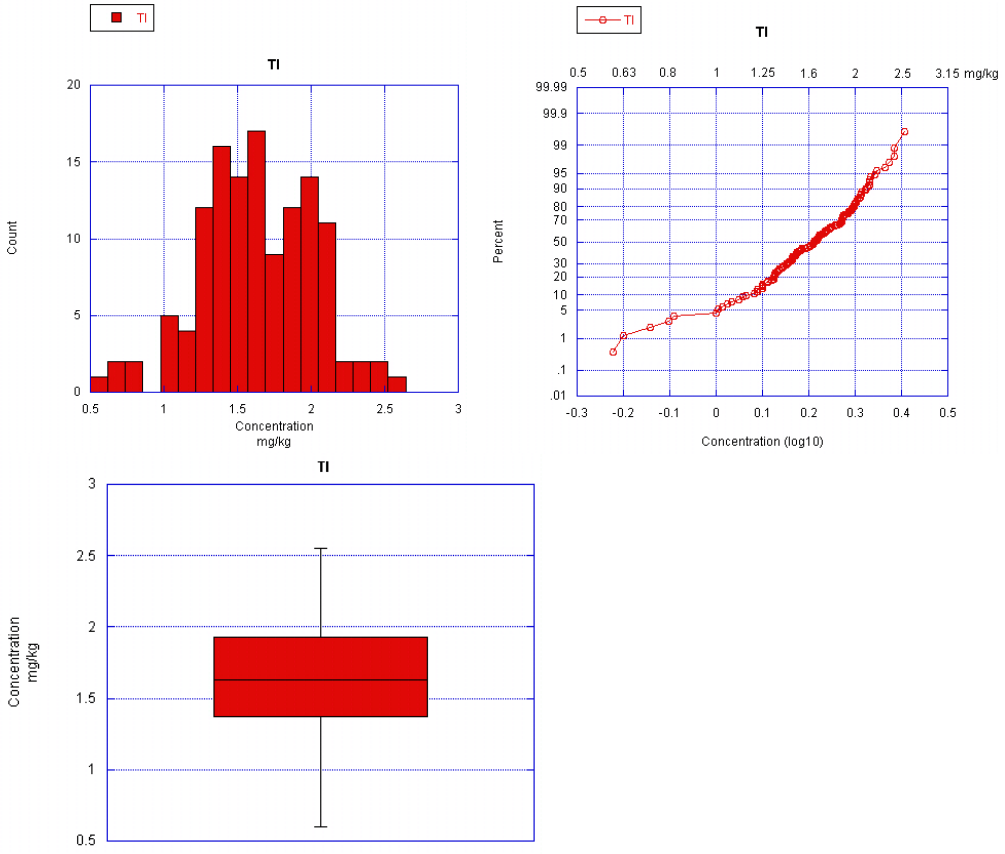
Into the environment thallium can spread by water mobilization from Tl-rich soils to groundwaters.

Thallium and its compounds are highly toxic. Human body can absorb thallium through skin, breathing organs and digestive tract, its uptake mainly occur after accidental contact or ingestion of rat poison. Poisoning effects are stomachaches and nervous systems damages and, in some cases even death. Chronic effects of thallium accumulation in human bodies are depressions, leg pains, hair loss, headaches, and lack of appetite.

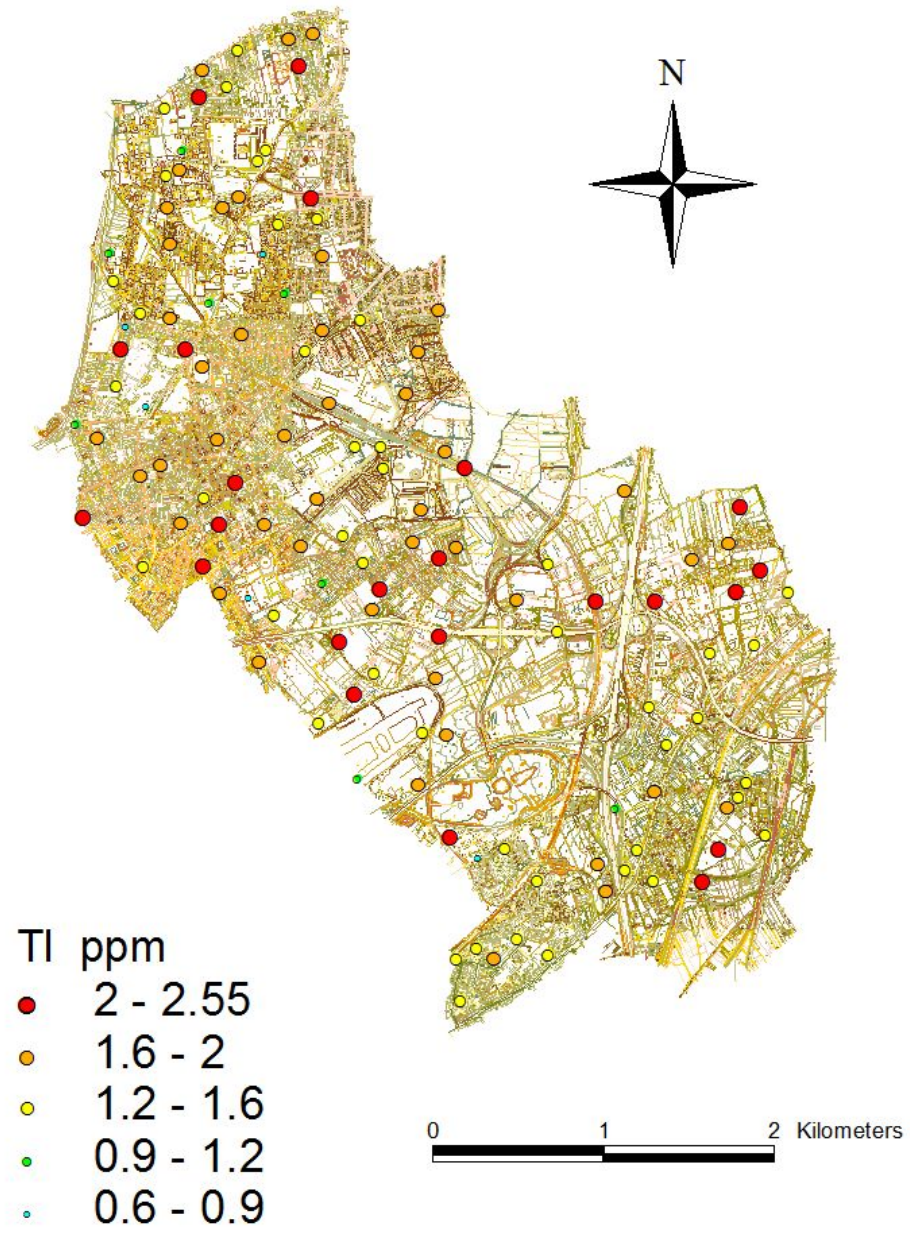
Distribution of Tl concentrationts

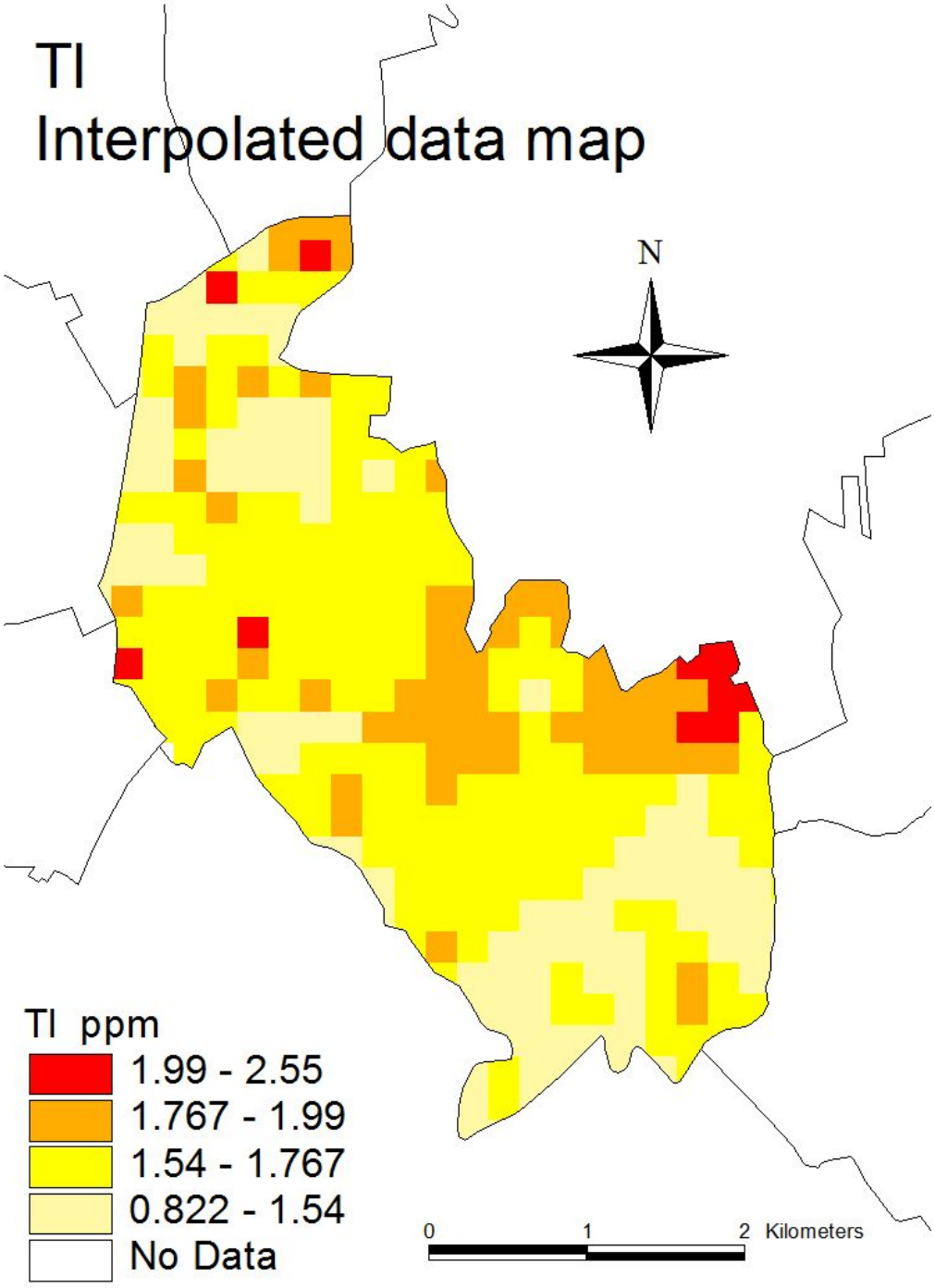
Value between 2-2.5 mg/kg are tipical in Casoria soils, and the highest Tl baseline values (1.6–2.4 mg/kg) correspond to the baseline value detected in Vesuvius volcanic lithologies, whereas the values between 0.4 and 1.7 mg/kg are tipical of the volcanic products of the Campi Flegrei volcanic field (1-1.7 mg/kg, Cicchella et al. 2005)..

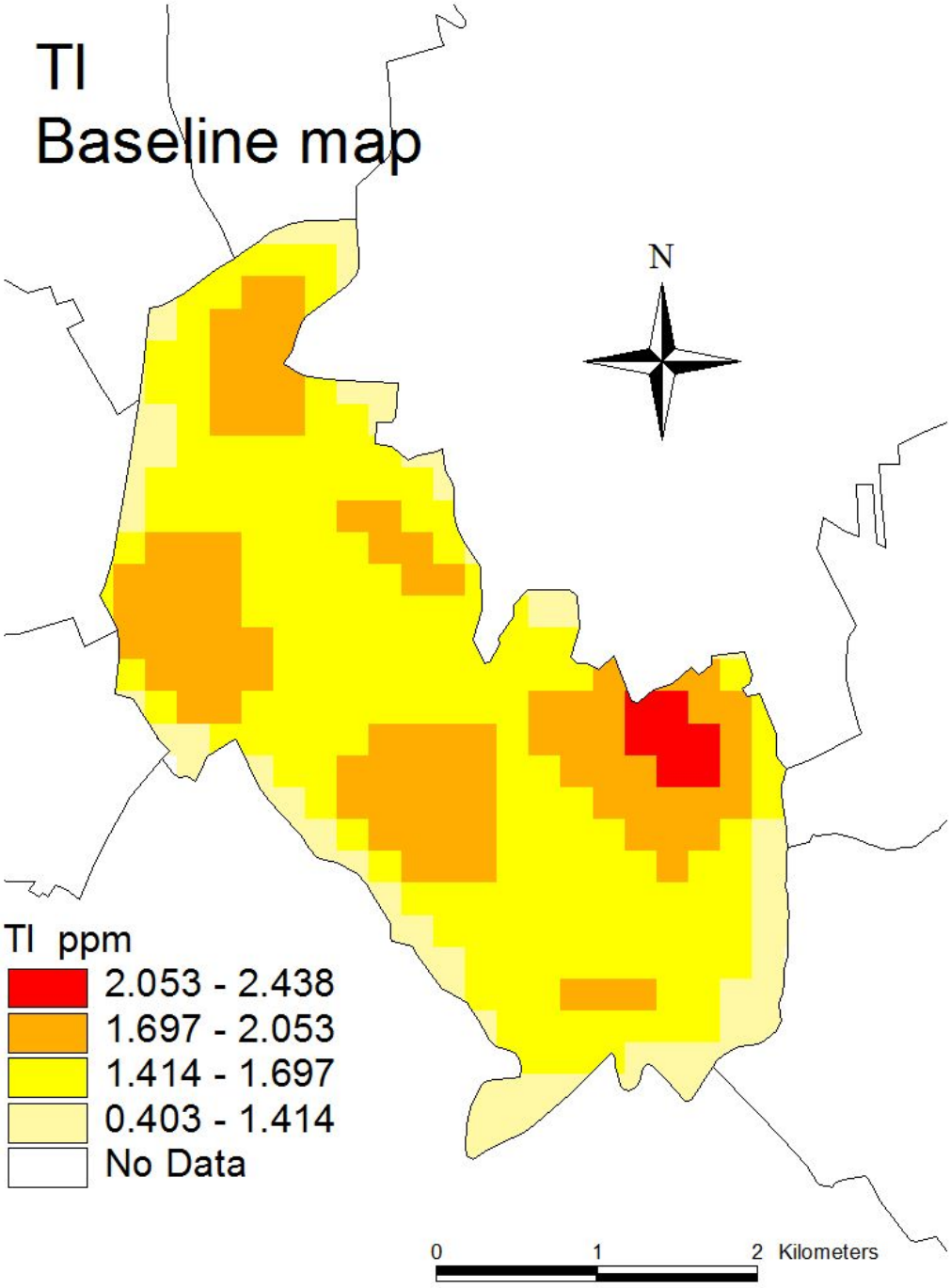
The control on the Tl spatial distribution, in the soils of the Comune di Casoria (as the entire Neapolitan territory), is strictly geogenic, and hence the spatial baseline values have to be considered coincident with natural background values.



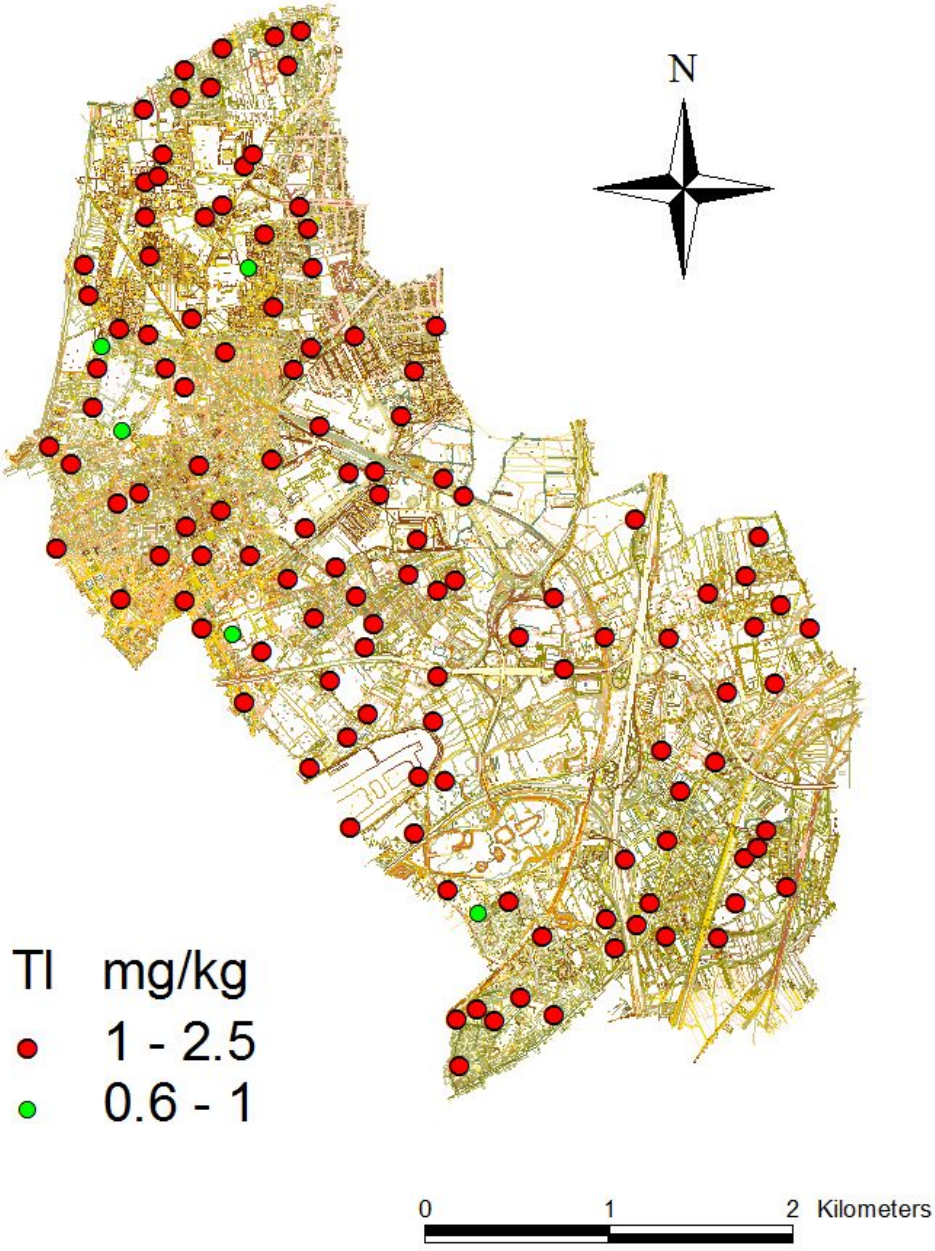
Tl
Dot Map




Tl
Interpolated data map
N
Tl ppm
1.99 - 2.55
1.767 - 1.99
1.54 - 1.767
0.822 - 1.54
No Data
0
1
2 Kilometers


Tl
Baseline map
N
Tl ppm
2.053 - 2.438
1.697 - 2.053
1.414 - 1.697
0.403 - 1.414
No Data
0
1
2 Kilometers

Tl
Risk map (D.Lgs. 152/06)
Residential threshold 1 mg/kg



Vanadium (V)

Vanadium is a metal mainly used to produce alloys.

Its alloys are used in jet engines and high speed air-frames, in nuclear reactors, in axles, gears crankshafts and other components.

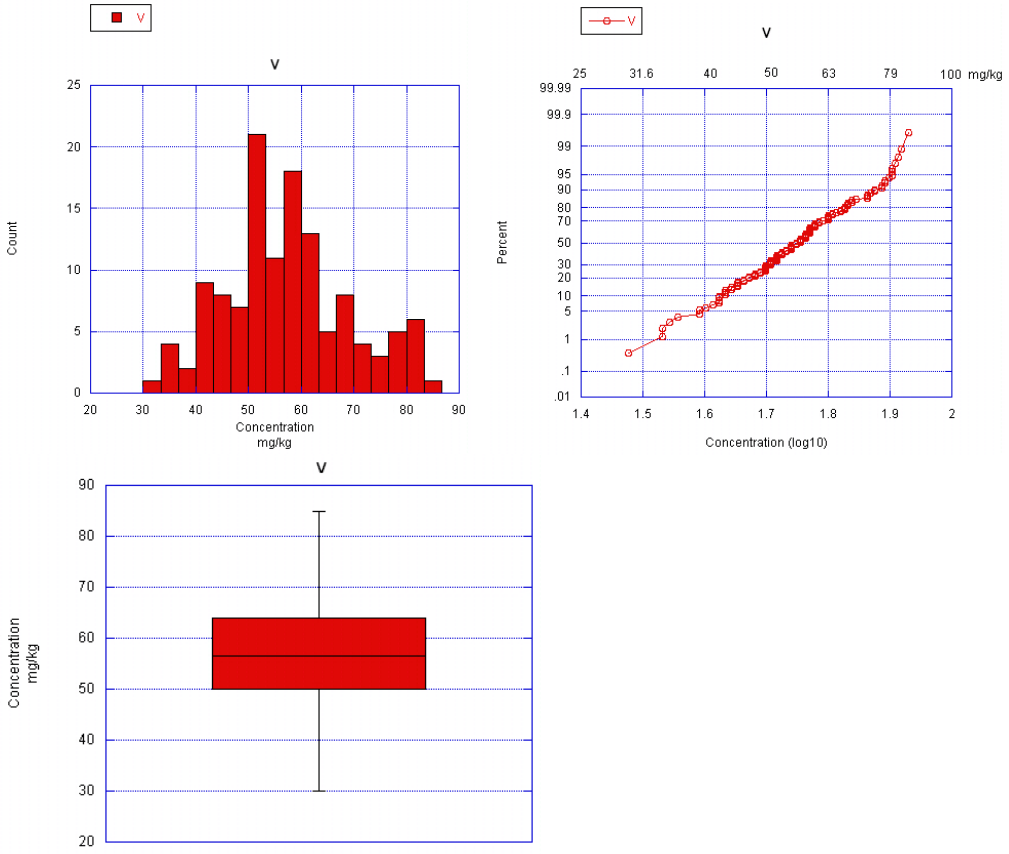
Vanadium occurs in many different minerals, the most famous of these are vanadinite, patronite, carnotite and bauxite. It's always obtained as a byproduct of other ores even if many vanadium ores are known.

Vanadium is contained even in large concentrations in most soils and, according to its availability, is absorbed by plants. Humans mainly uptake vanadium through food; the vanadium richest are soya, beans, eggs, apples, olive oil and sunflower oil.

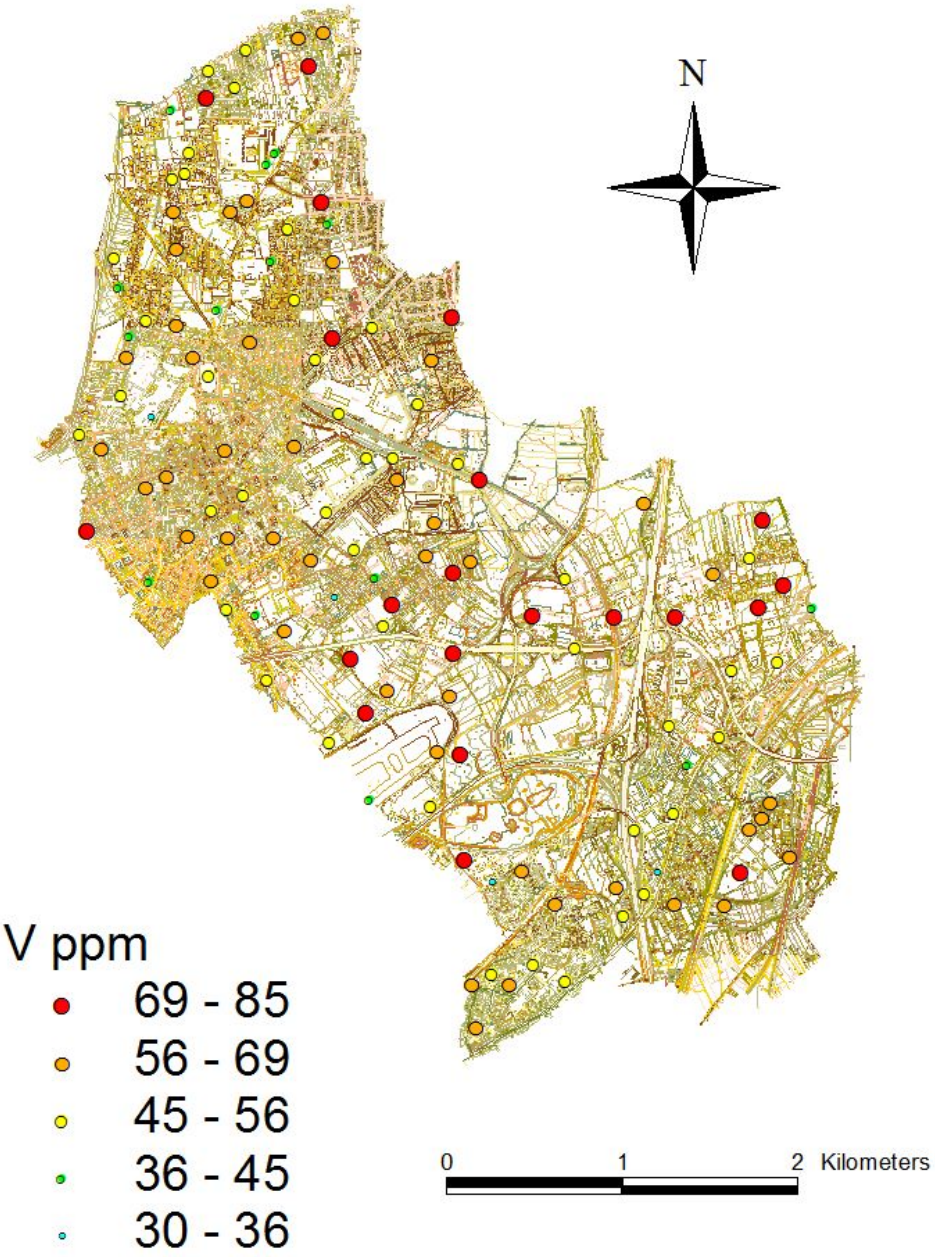
Vanadium effects on human health, for high exposure, are bronchitis and pneumonia, irritation of lungs, throat, eyes and nasal cavities, cardiac and vascular disease, inflammation of stomach and intestines, damage to the nervous system, bleeding of livers and kidneys, severe trembling and paralyses, weakening, and headaches.

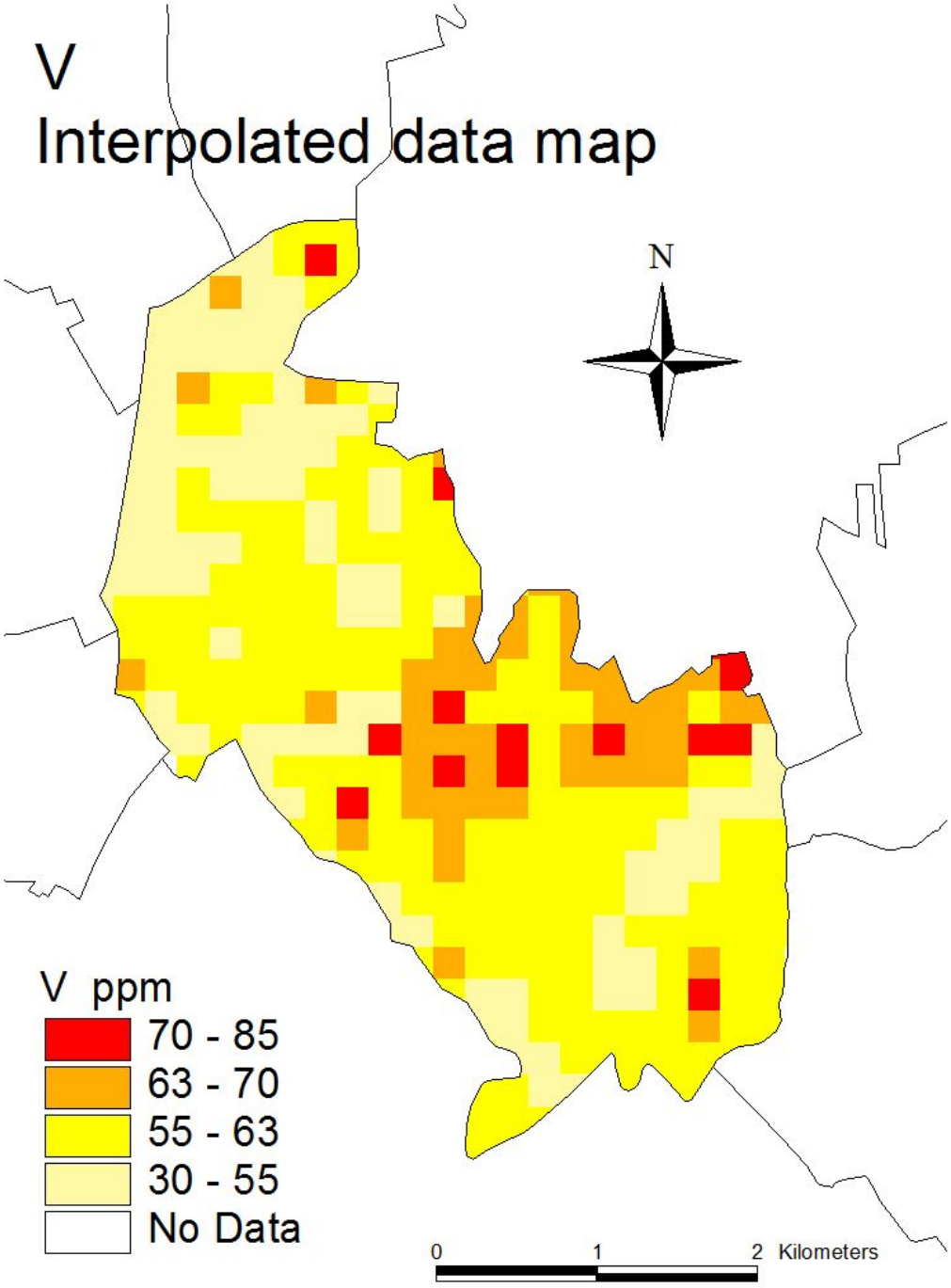
Distribution of V concentrationts

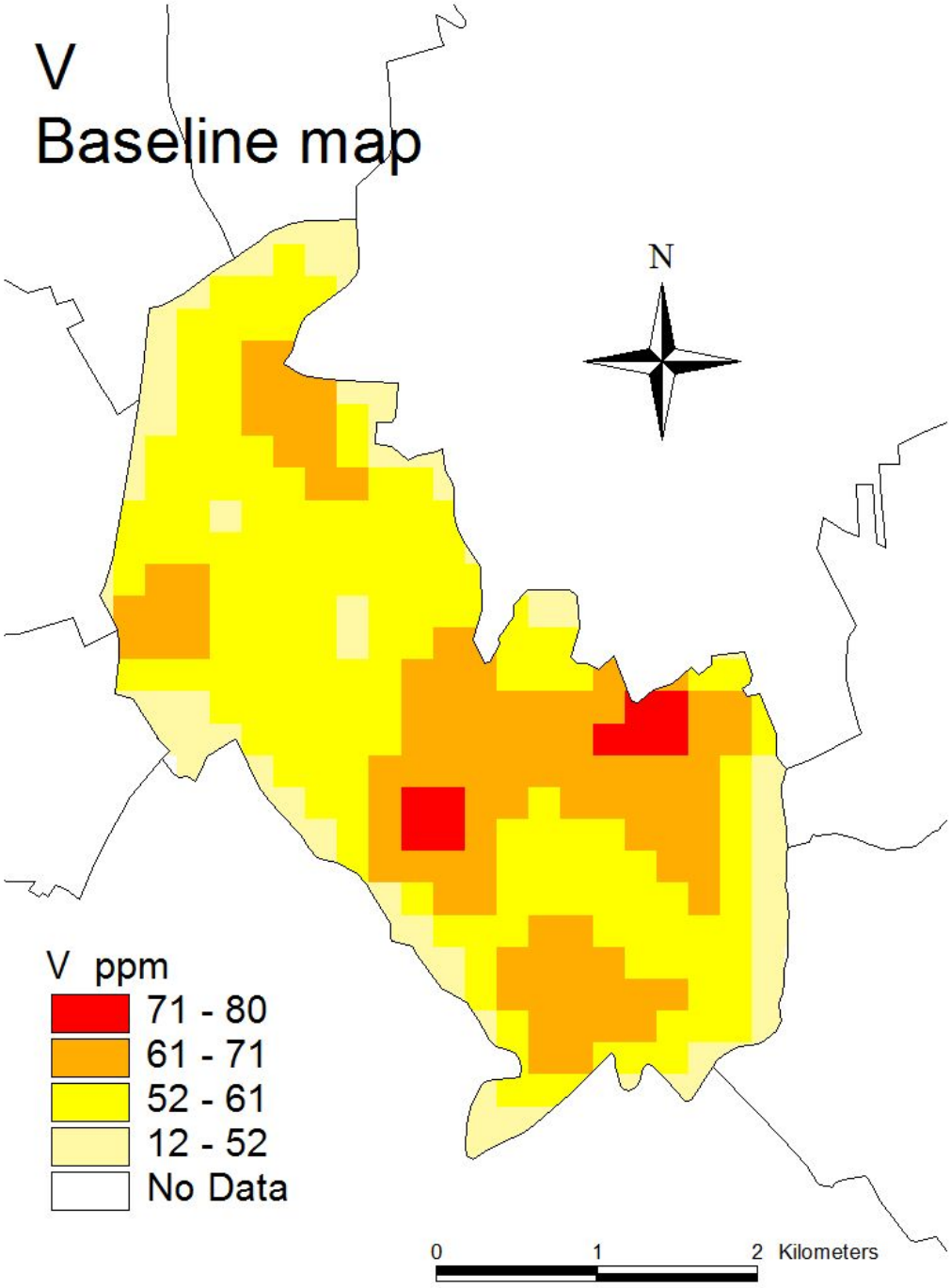
V higher value (69-85 mg/kg) are founded in the southern sector of Casoria municipal area near international airport fields, and in the same area highest baseline values (71-80 mg/kg) occurs; The baseline values in the range 60–120 mg/kg are mostly geogenic (Cicchella et al. 2005), but at least locally, some high values might be influenced by anthropogenic activities (airport activity). At least is possible to consider Casoria soils values in the natural background concentration range, that is evalueted 30–120 mg/kg.



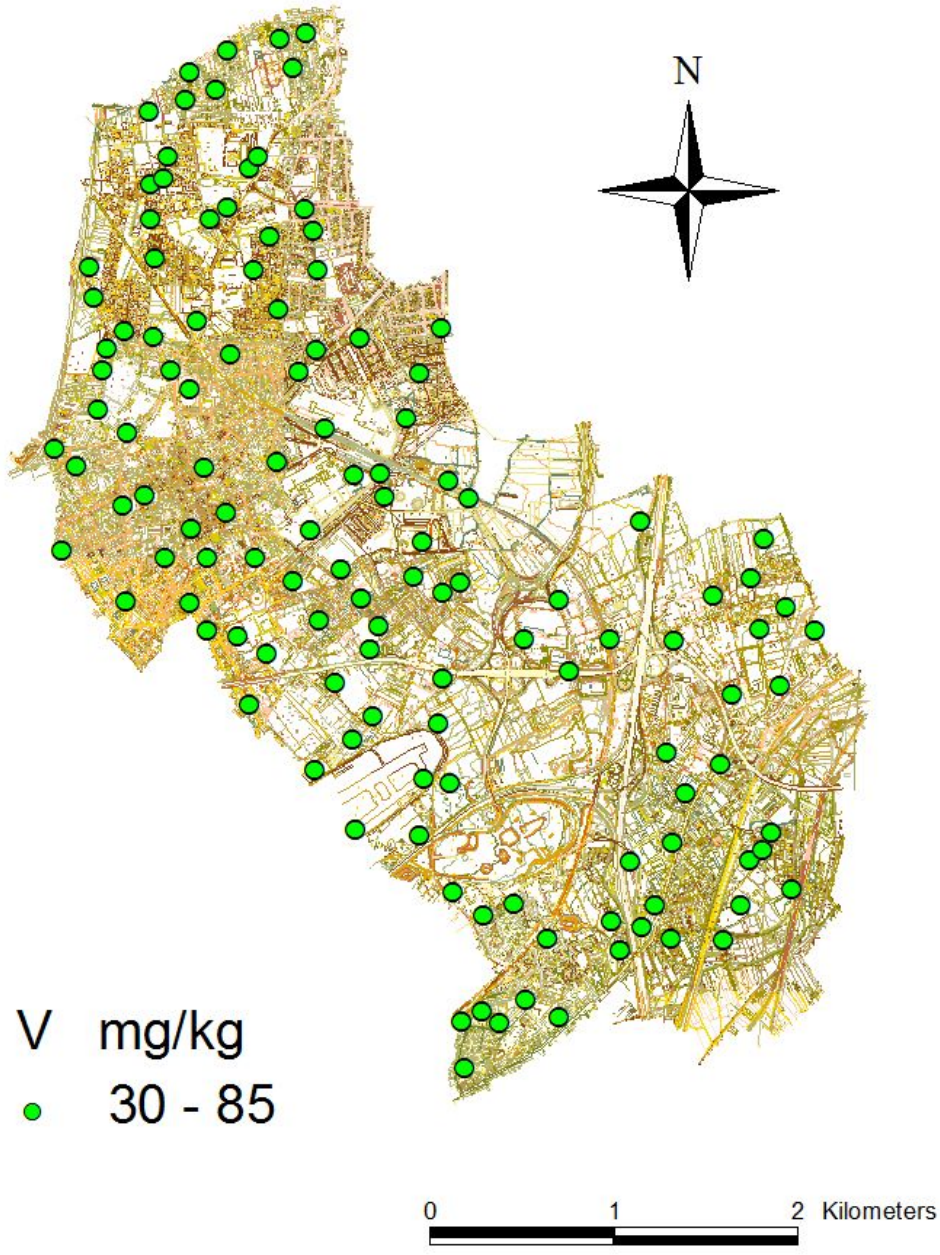
V
Dot Map




V
Interpolated data map
N
V ppm
70 - 85
63 - 70
55 - 63
30 - 55
No Data
0
1
2 Kilometers


V
Baseline map
N
V ppm
71 - 80
61 - 71
52 - 61
12 - 52
No Data
0
1
2 Kilometers

V
Risk map (D.Lgs. 152/06)
Residential threshold 90 mg/kg



Zinc (Zn)

Zinc is a metal used in many and different fields: from coins to gutters, from iron galvanization to paints, from cosmetics to photocopier paper.

Its main ore is the blende (or sphalerite), but also smithsonite and hemimorphite; its major mining districts are Russia, USA, Canada, Australia and Peru.

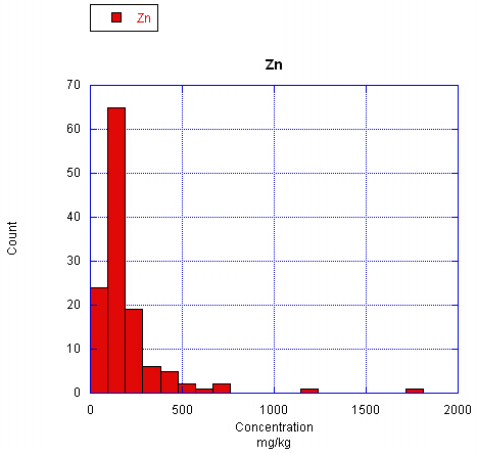
Zinc naturally occurs in many foodstuffs and in drinking water. In soils, air and waters, it can be naturally found, but human activities such as coal and waste combustion, mining and steel production, may be sources of zinc contamination.

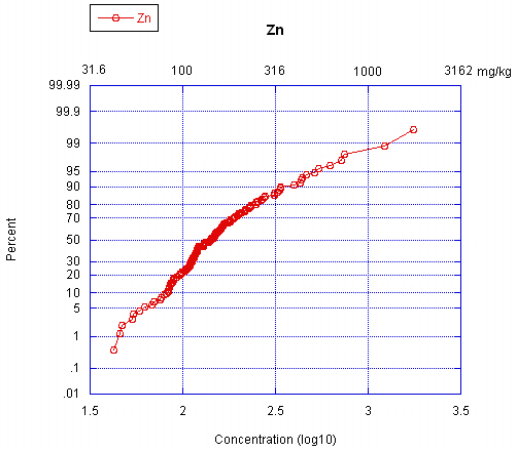
It is a trace element essential for human health and, therefore, people with zinc shortages can have some problems, such as loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. On the other hand, too much zinc can cause health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia, but also pancreas damages and arteriosclerosis.

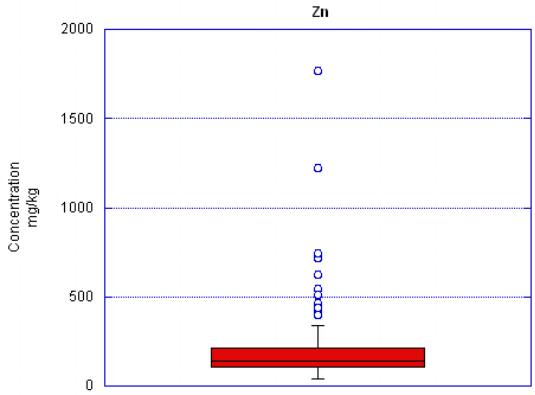
Zinc can contaminate rivers and seas when released by industries into the wastewaters; as a consequence, acidity of waters increases, and water organisms may accumulate it in their bodies. Some fish uptake zinc from waters and bio magnify it up the food chain. Animals and plants living on Zn-rich soils can also uptake it and this negatively influences the plants diversity because only few species of them can survive high Zn accumulation. The presence of large zinc contents in soils can also interrupt the activity of microrganisms and earthworms, thus causing serious problems to the evolution of the soil itself.

Distribution of Zn concentrationts

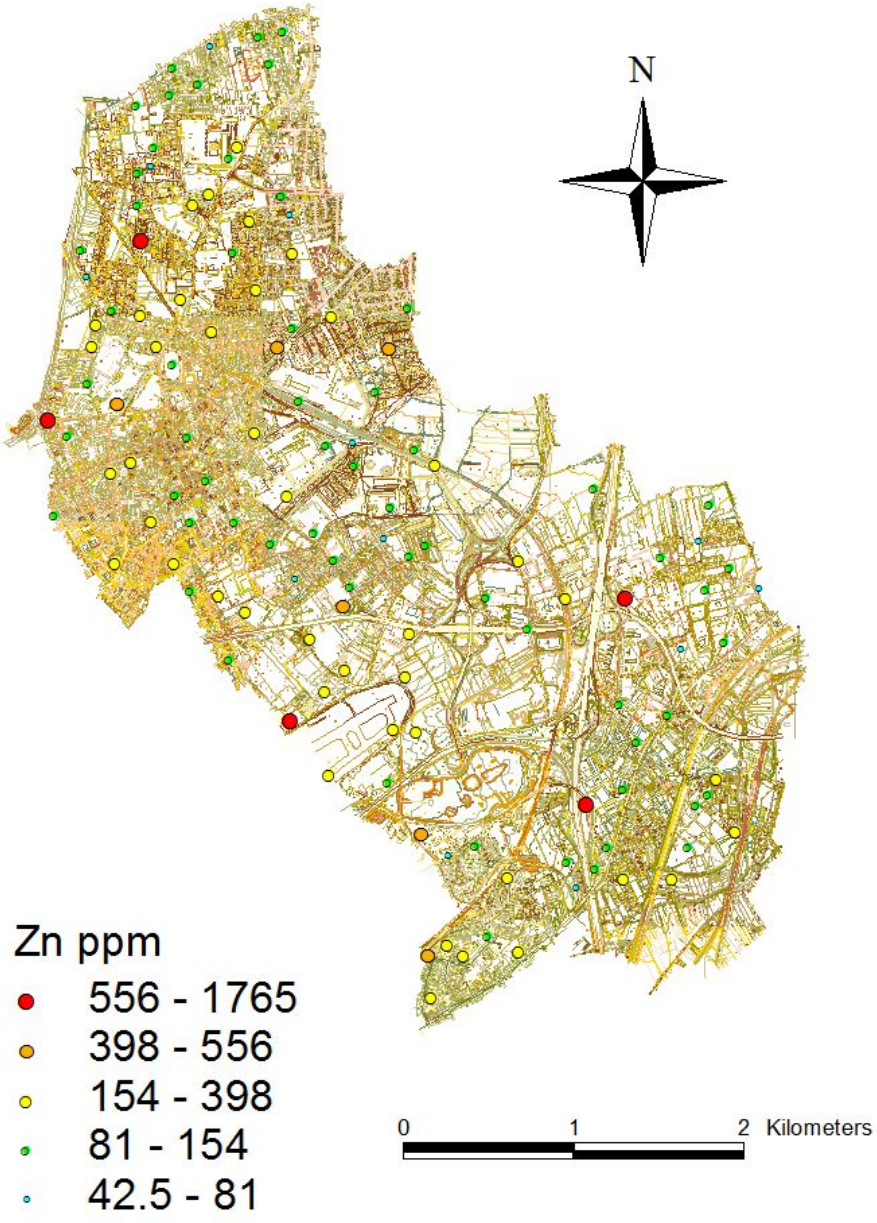
Zn higher values samples (400-1765 mg-kg) are located in the western sector of Casoria territory. Distribution of baseline values matches quite well with the Cd-Pb distribution, in which higher Zn values (200–400 mg/kg) correspond to the mostly urbanized territory and the City of Naples border. In this areas, there is a clear anthropogenic influence on the Zn baseline distribution. Most of the soils of the suburban areas show concentrations in the range 23– 125 mg/kg, which is identified as natural background values (Cicchella et al. 2005).

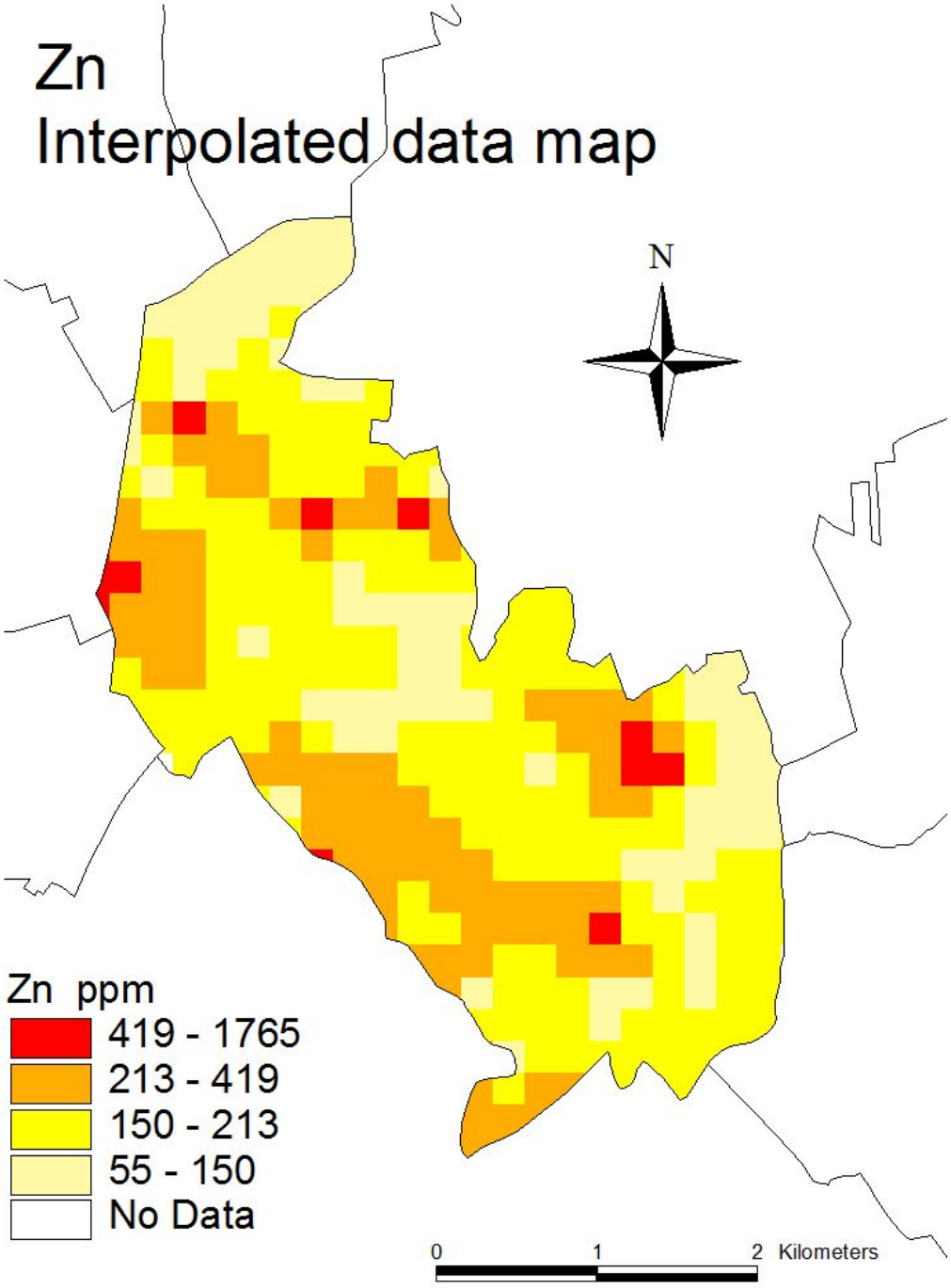

Zn
Zn
Count
Concentration
mg/kg

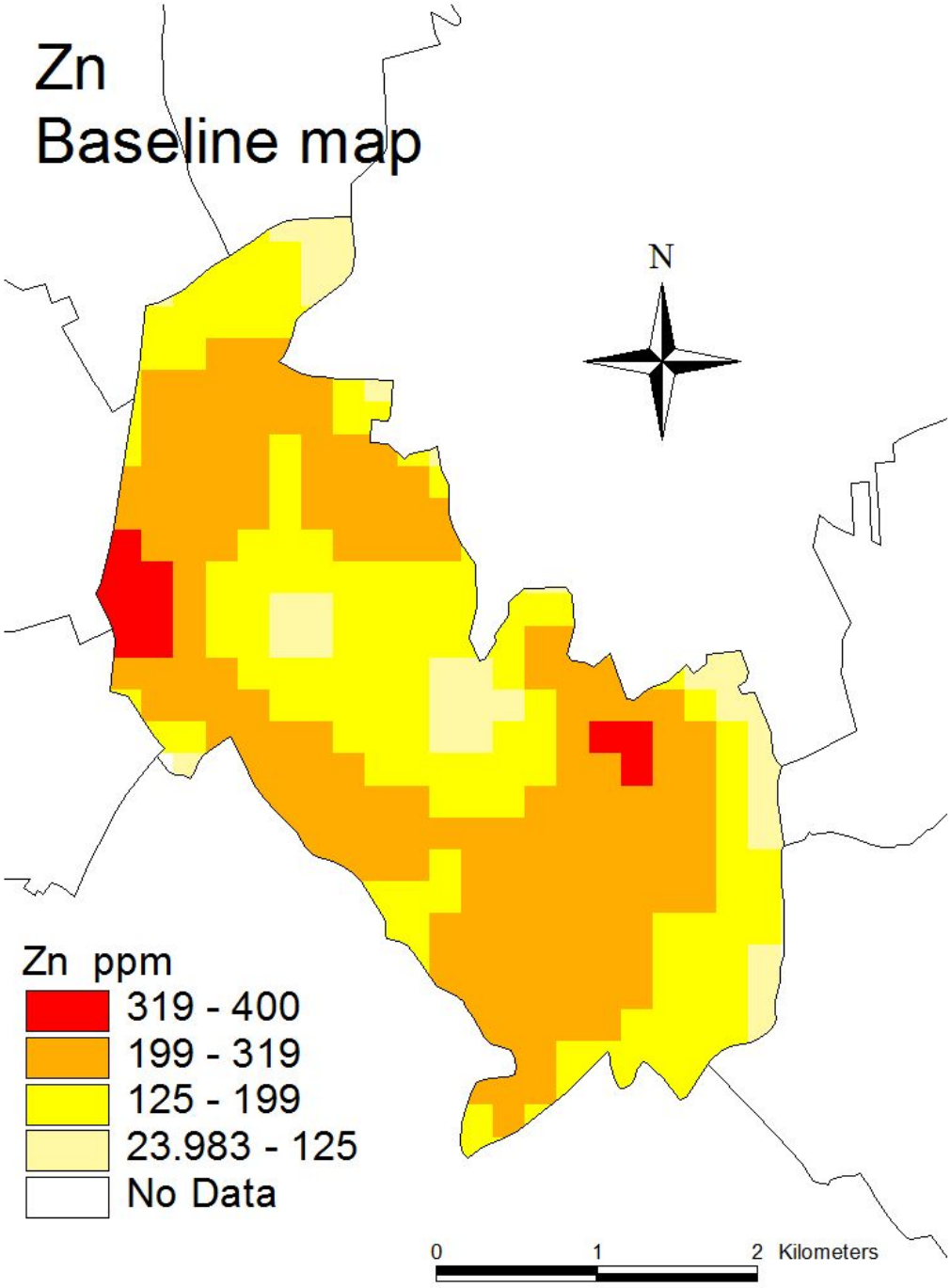

Zn
Zn
31.6
100
316
1000
3162 mg/kg
Percent
Concentration (log10)


Zn
Concentration
mg/kg

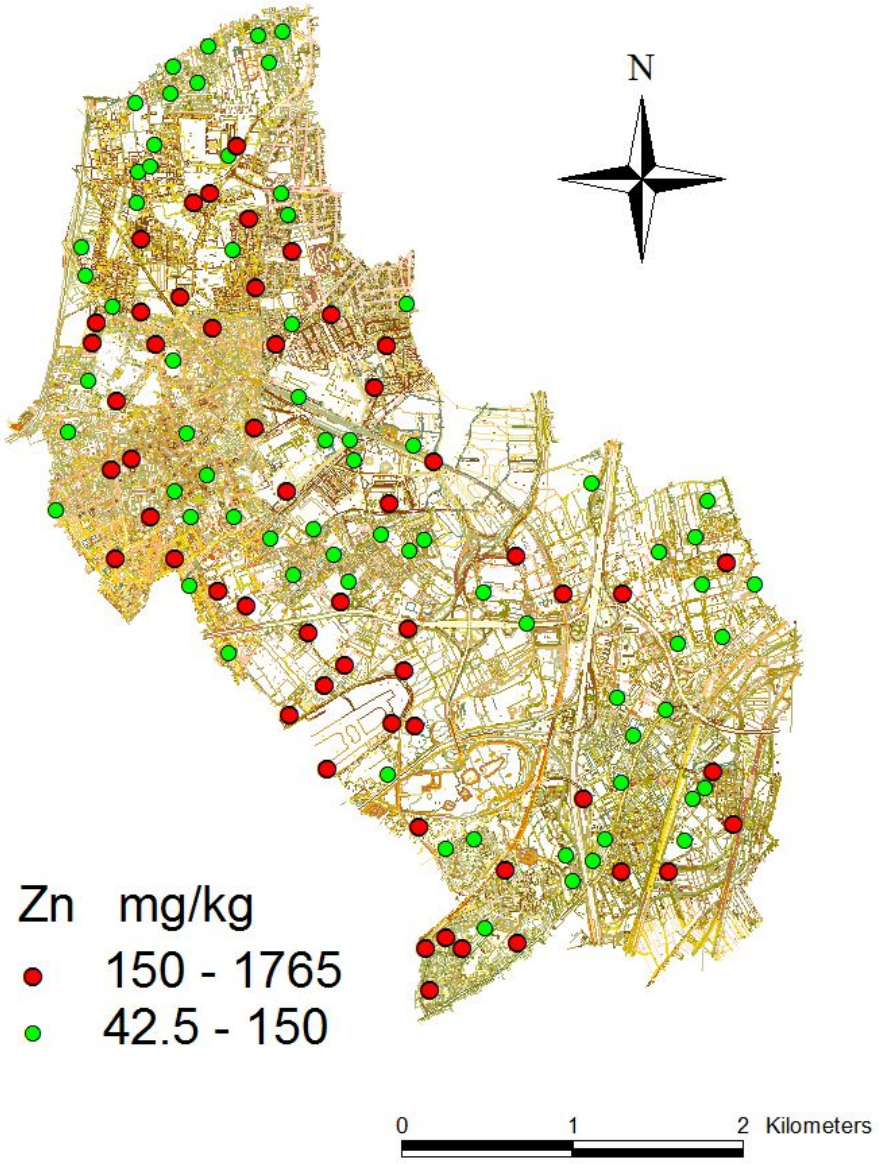
Zn
Dot Map




Zn
Interpolated data map
N
Zn ppm
419 - 1765
213 - 419
150 - 213
55 - 150
No Data
0
1
2 Kilometers


Zn
Baseline map
N
Zn ppm
319 - 400
199 - 319
125 - 199
23.983 - 125
No Data
0
1
2 Kilometers

Zn
Risk map (D.Lgs. 152/06)
Residential threshold 150 mg/kg



6 Isotopic ratios

The Pb isotopic ratios obtained from TIMS analysis for surface soils, soil profiles, has been plotted. on the X-Y axis of graphs shown in Figures 13 – 19. In this work has been reported the 208Pb/207Pb - 206Pb/207Pb and 208Pb/204Pb – 206Pb/204Pb ratios of our samples and those representing the isotopic signature from three of the pesticides most commonly used in the studied area: Azin Pb30, Crittam WG and Cosan's (Grezzi et al., 2010). As end-members of these plots, have been chosen literature data of both geologic and anthropic sources, such as the volcanic related deposits from Vesuvius activities (Ayuso et al., 1998) and Yellow Tuff (D'Antonio et al., 1995, 2007) the gasoline (Monna et al., 1997-1999; Chiaradia et al., 1999), the aerosol deposits (Monna et al., 1999; Tommasini et al.,2000, Geagea et al., 2008) Bagnoli ex industrial brownfield soils (Tarzia et al 2002) and Neapolitan soils (Cicchella et al.2008) .

6.1 Surface soils

Surface leached samples have an isotopic composition closer to the Pb signature in aerosol,and Ex-Italsider brownfield area soils (Naples), only CAS004 soil sample shows an isotopic composition closer to bedrock composition (Fig. 13).

Casoria superficial soils present the same trend of Neapolitan soils mainly controlled by anthropic activities due to the high urbanization and industrialization (Fig. 14).

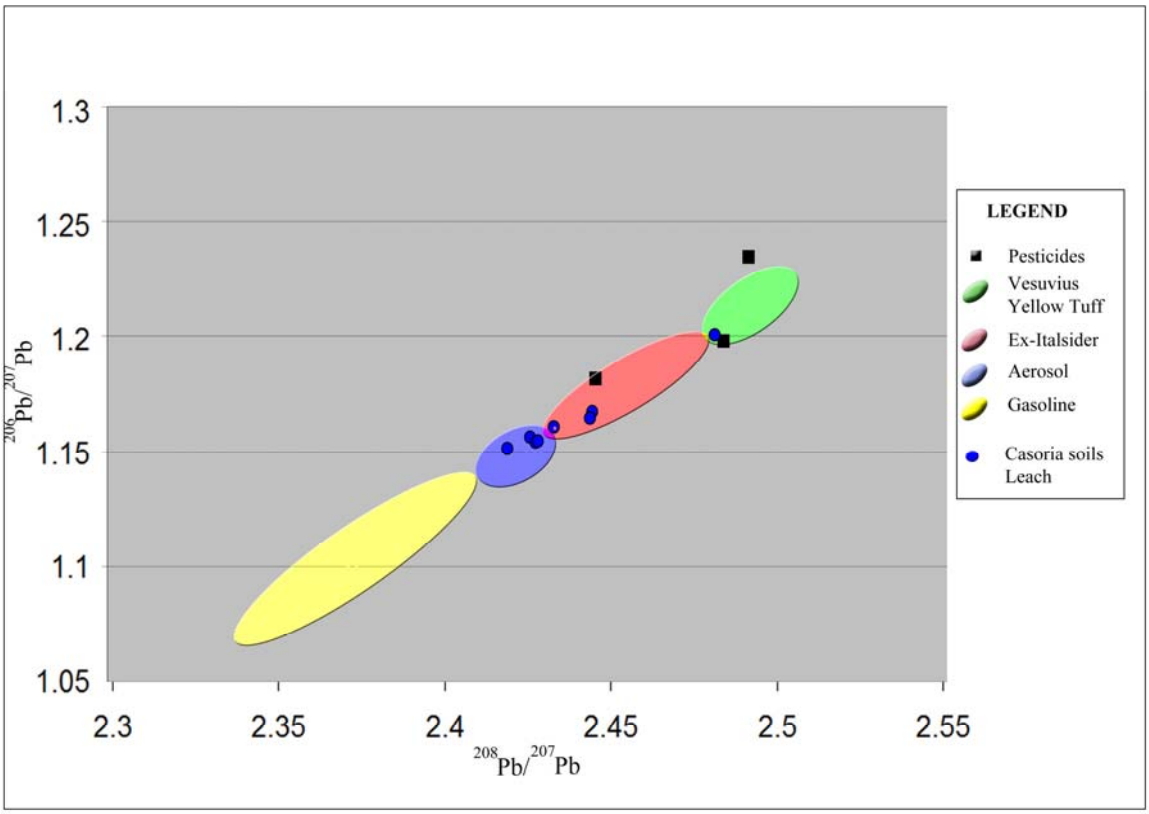


Figure 13 Casoria Surface soil isotopic ratio. Vesuvius (Ayuso et al. 1998), Yellow Tuff (D'Antonio et al. 2010), Ex Italsider (Tarzia et al.2002), Aerosol (Geagea et al 2008, Tommasini et al. 1999, Monna et al.1997) Gasoline (Monna et al. 1997, Chiaradia et al, 1999)

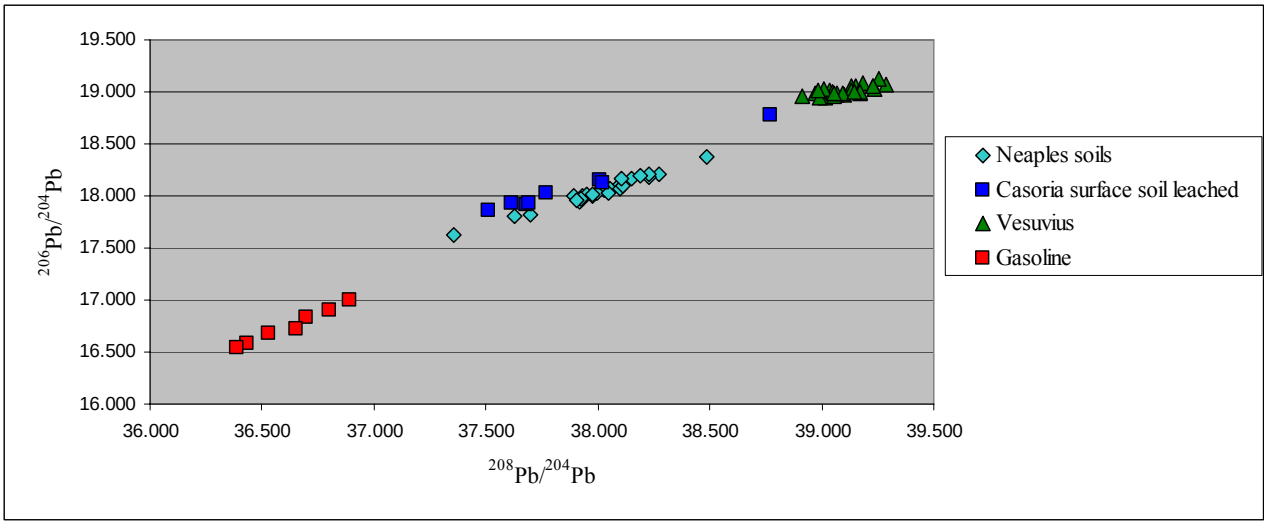


Figure 14 Casoria surface soils isotopic ratio. Vesuvius (Ayuso et al. 1998), Gasoline (Monna et al. 1997) Naples soils (Cicchella et al. 2008)

6.2 Soil profile (0-10 cm)

Figure 15 shows the isotopic ratios for all 5 soil profiles collected for a deep of 0-10 cm. Leached and residue Pb ratios overlap each other but they follow a regular trend in which residues are shifted toward the geologic signature and leached are closer to the aerosol area.

This profile superficial level shows the same trend of surface soils: isotopic imprinting typical of Neapolitan urbanized and industrialized (ex-italsider) areas (Fig. 16).

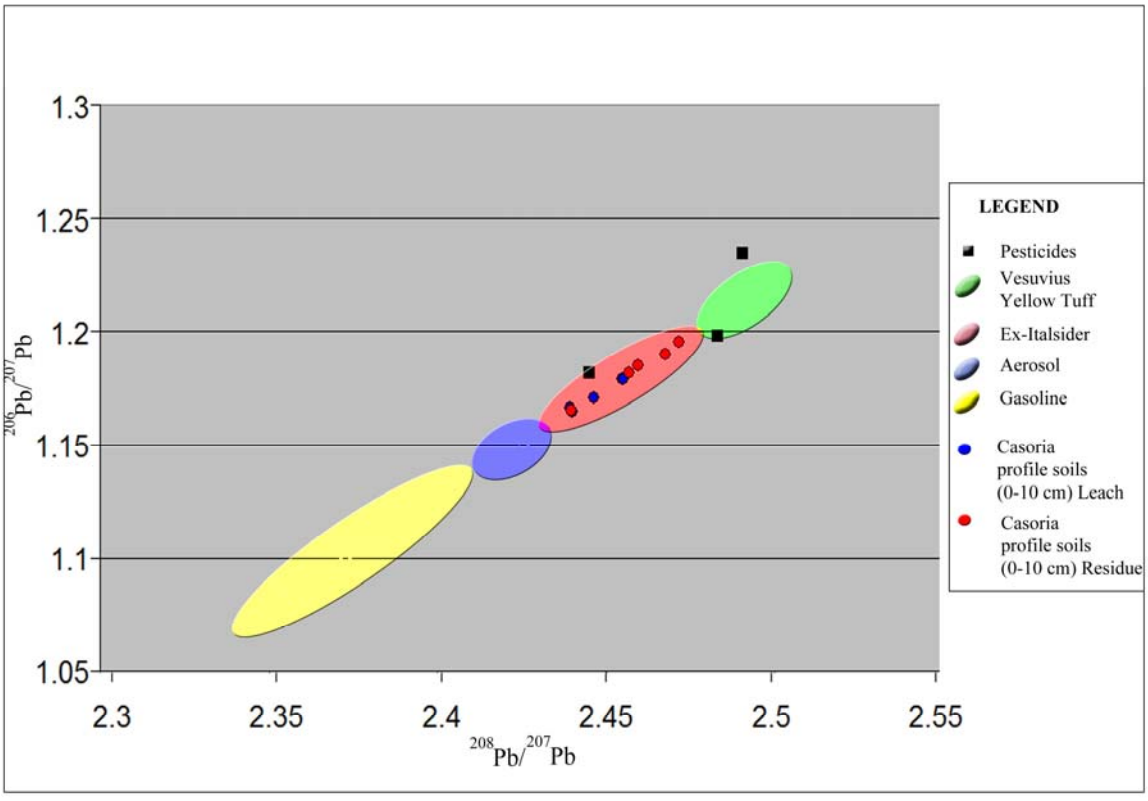


Figure 15 Casoria Profile soils (0-10 cm) isotopic ratio

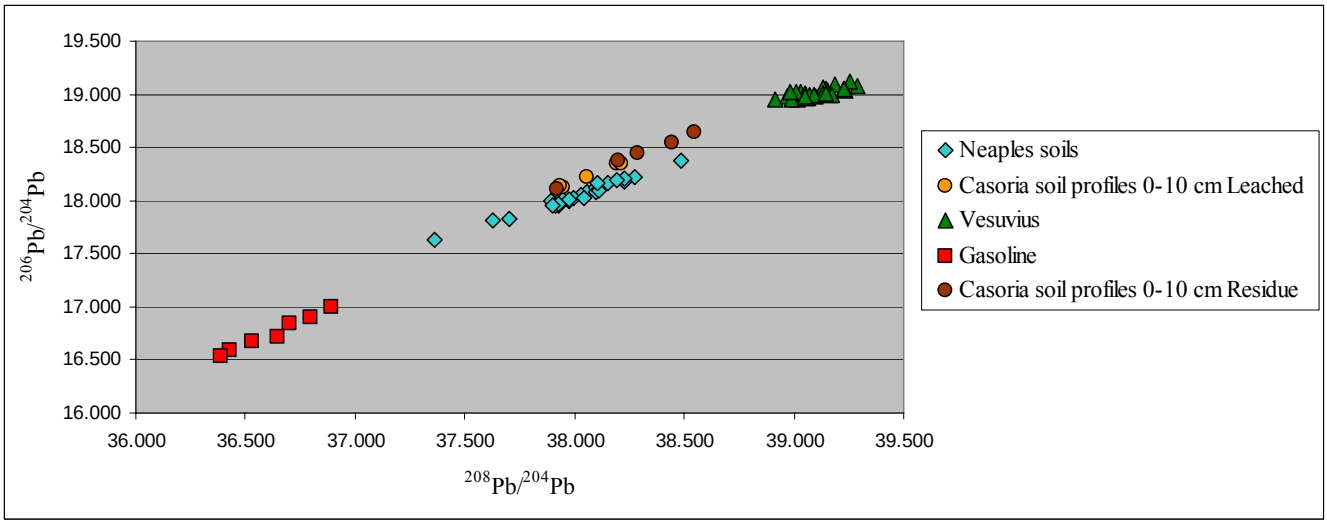


Figure 16 Casoria Profile soils (0-10 cm) isotopic ratio

6.3 Soil Profile (90-100 cm)

Figure 17 shows the isotopic ratios for all the soil profiles collected for a deep of 90-100 cm. Residues were analized only for three profile samples (# 1-2-3). Leached and residue Pb ratios shows a similar trend with Profile samples (0-10 cm); isotopic ratios overlaps each other but they follow a regular trend in which residues are shifted toward the geologic signature and leached are closer to the aerosol area.

Analyzed samples taken in the deep soil horizon, are mainly concentrated in the same field of surface soils, it is possible that the contamination is leached from the surface to the deepest level (Fig. 18).

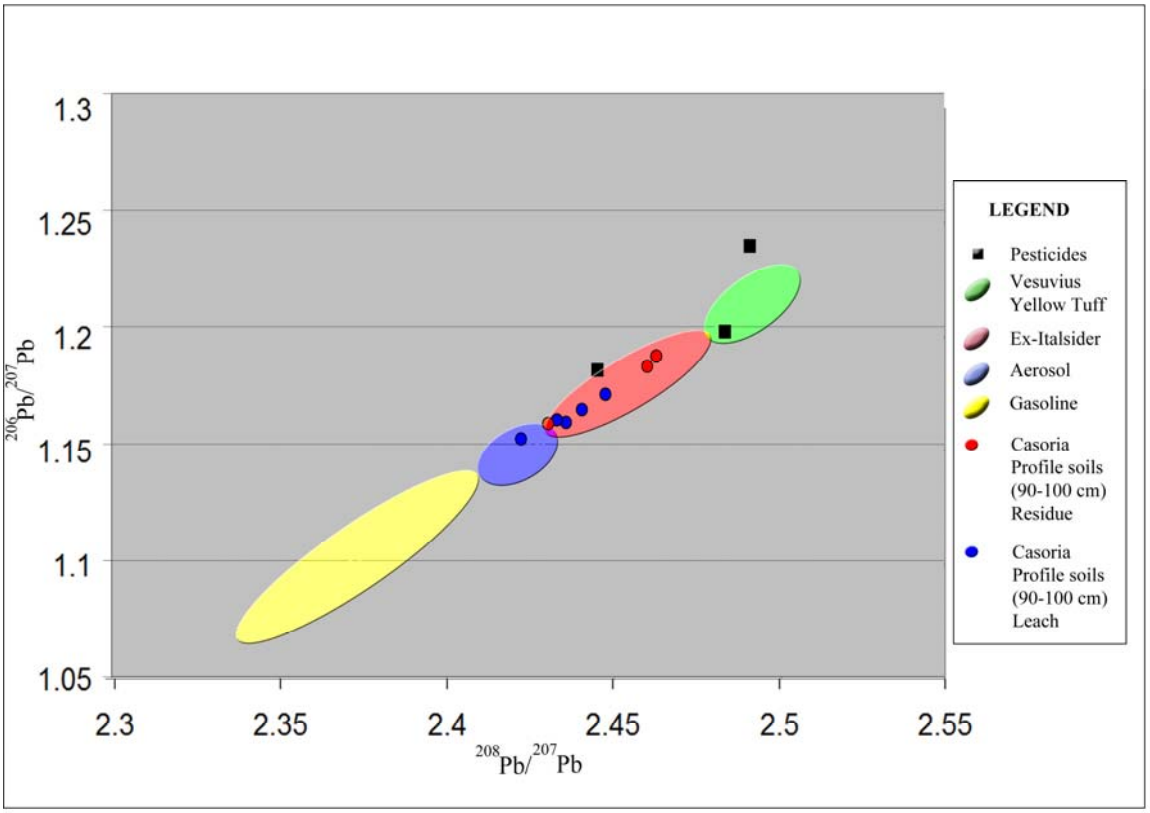


Figure 17 Casoria Profile soils (90-100 cm) isotopic ratio

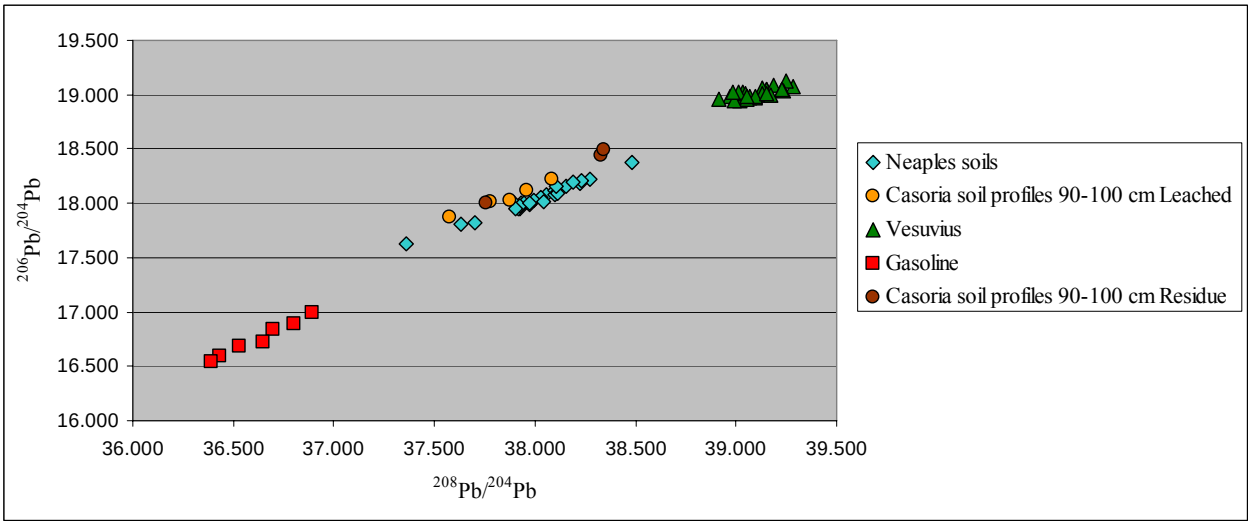


Figure 18 Casoria Profile soils (90-100 cm) isotopic ratio

6.4 Tap water samples

Tap water used in Comune di Casoria, has origin from Serino water springs (Avellino province) located in Campanian Appennins. The same water is used in all Neapolitan area.

Due to the old and damaged water tube system condition, tap water is sampled to control if lead imprinting is mostly geogenic or anthropogenic.

This pilot study is preliminary to further analysis on tap water in Neapolitan and southern Casertan polluted areas and on spring waters to demonstrate if what people drink, use to cook and clean is healthy or potentially dangerous.

To obtain 750 ml of filtered water from each sample, a total of 100 Millipore filters with a mesh of 0.4 mm were used.

Lead ratios have been measured on filtered waters and the presence of such anthropic Pb ratio values in the samples, could be the evidence of a high interaction between water surface and aerosols, due to the damaged tube system which not guarantee the tap water quality (Fig. 19). Previously work on surface waters and groundwaters of Agro-Aversano and Domitio Littoral showes the same isotopic ratio imprinting, evidence of the high solubility of anthropogenic Pb in waters.

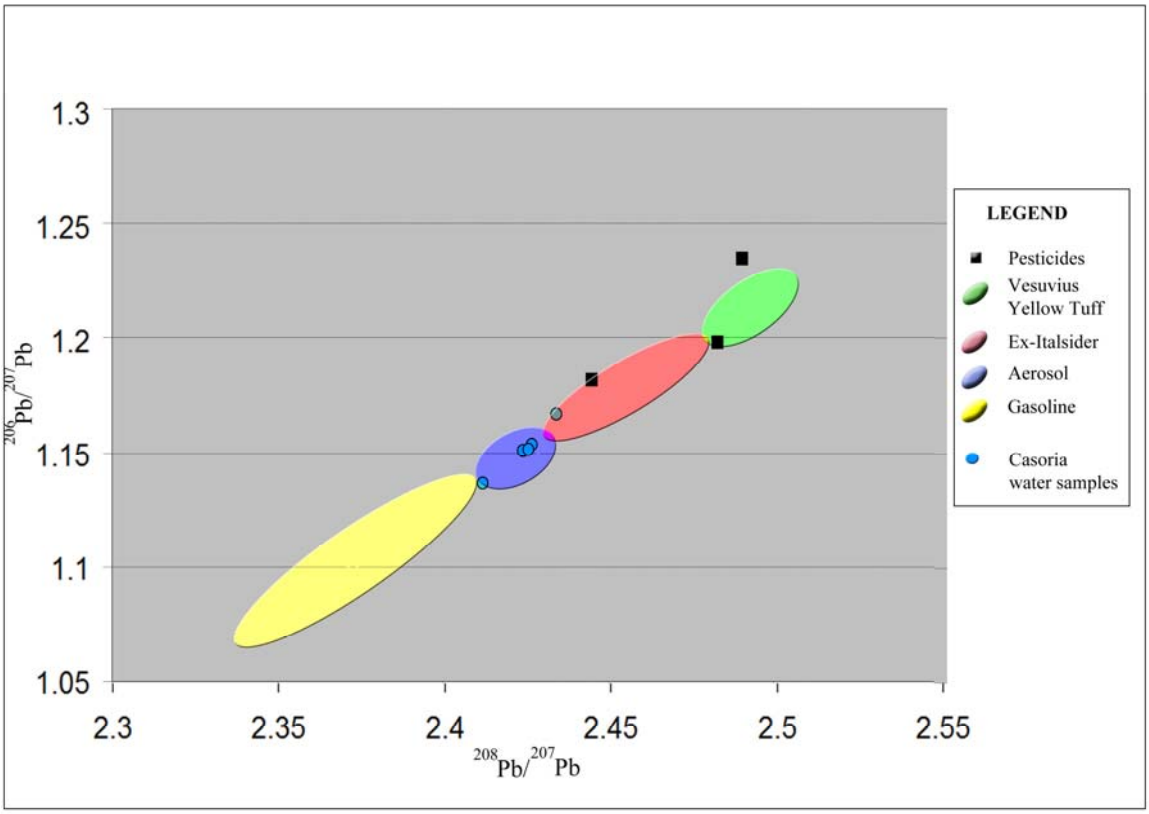


Figure 19 Casoria tap water isotopic ratio

7 Conclusion

The environmental geochemistry study in the Comune di Casoria was carried out through sampling of superficial soils, profile soils and tap water..
Based on the areal distribution of the potential harmful elements in the soil, was then carried out a study of Pb isotopes to discriminate the natural component than the anthropic one.

The isotopic study has proved very useful in soils where the concentrations of metallic elements may be due to both factors, litogeological ones, for soils developed on volcanic rocks, anthropic ones, in soils closed urban and industrial activities.

The distinction between the natural and anthropogenic contamination has important practical consequences because when it was shown that the source of the contamination is natural, safety procedure and remediation activities are not necessary if exceeding the limits imposed by the D.Lgs. 152/06 for both residential and industrial use. Following work was therefore carried out in different phases and the results are discussed below.

Potential harmful elements in the Casoria area can be divided in three main different groups on the basis of their spatial distribution and correlation:

- Pb, Zn, Cd, Hg, Be highest concentration (Be 6.5-8.4 mg/kg, Cd 1.4-3.5 mg/kg, Hg 0.5-0.9 mg/kg, Pb 436-821 mg/kg, Zn 556-1765 mg7kg) are principally located in correspondence with the highest urbanized sector of Casoria, along the shared administrative boundary with the city of Napoli..
- V, Cu, Cr, Ni are mostly found on the southern sector of Casoria in correspondence with the residential area of the Arpino village. Highest concentration range: Cr 54-486 mg/kg, Cu 314-1034 mg/kg, Ni 27-70 mg/kg, V 69-85 mg/kg.
- As, Sn, Tl, Co present distribution patterns are usually spatially correlated with the volcanic features of the underlying geology (Neapolitan Yellow Tuff and loose pyroclastic deposits, locally reworked).

Basically the geochemical elemental distribution in soils of the Casoria territory follows the same rules found by Cicchella et al (2008) in the whole Neapolitan province.

Assumed that in the urbanized and industrialized areas of the Neapolitan province Pb content is mainly anthropogenic (Cicchella et al., 2008) it is possible to use Pb as a fingerprint of contamination. Comparing Pb values with other elements, trough out the use of scatter plot, if a positive correlation exists and it is significant, elements are considered to be mostly anthropogenic. If a negative correlation exists between Pb and an element a potential geologic origin can be considered for the element distribution. In the latter case, the element, .negatively correlated with Pb, is compared throughout a scatter plot, with Tl or As which are assumed to be basically geogenic (Cicchella et al., 2008; Albanese, 2008).

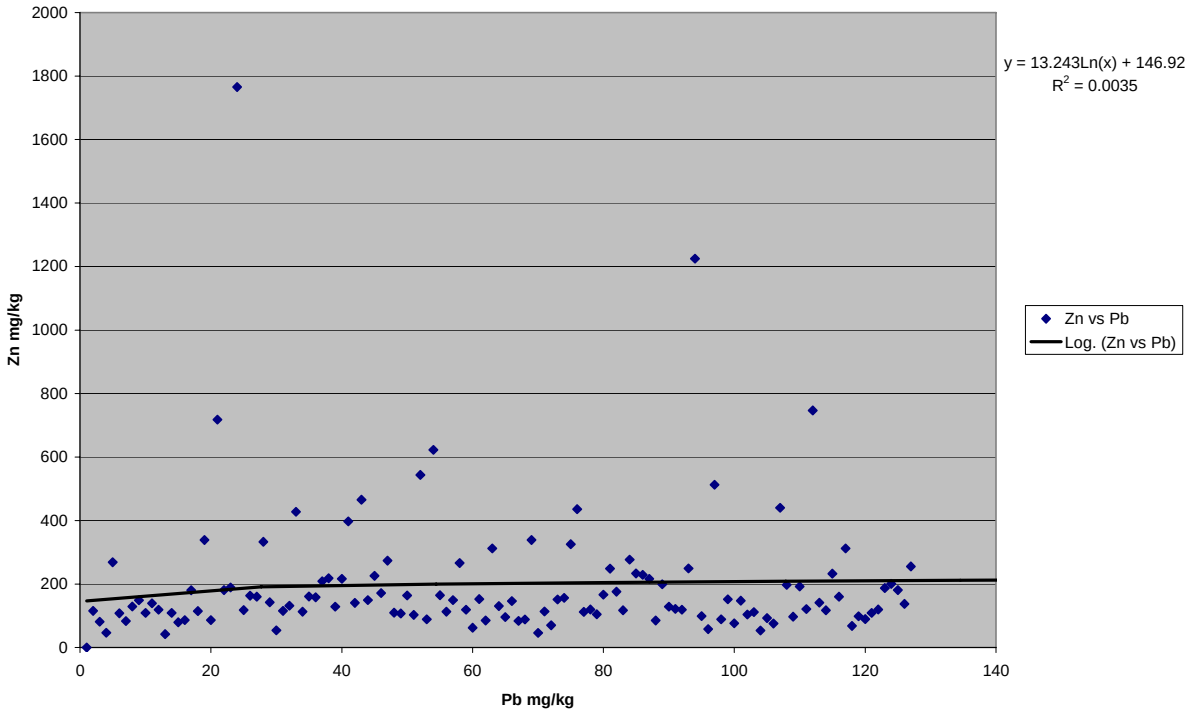


Figure 20 Pb vs Zn scatter plot

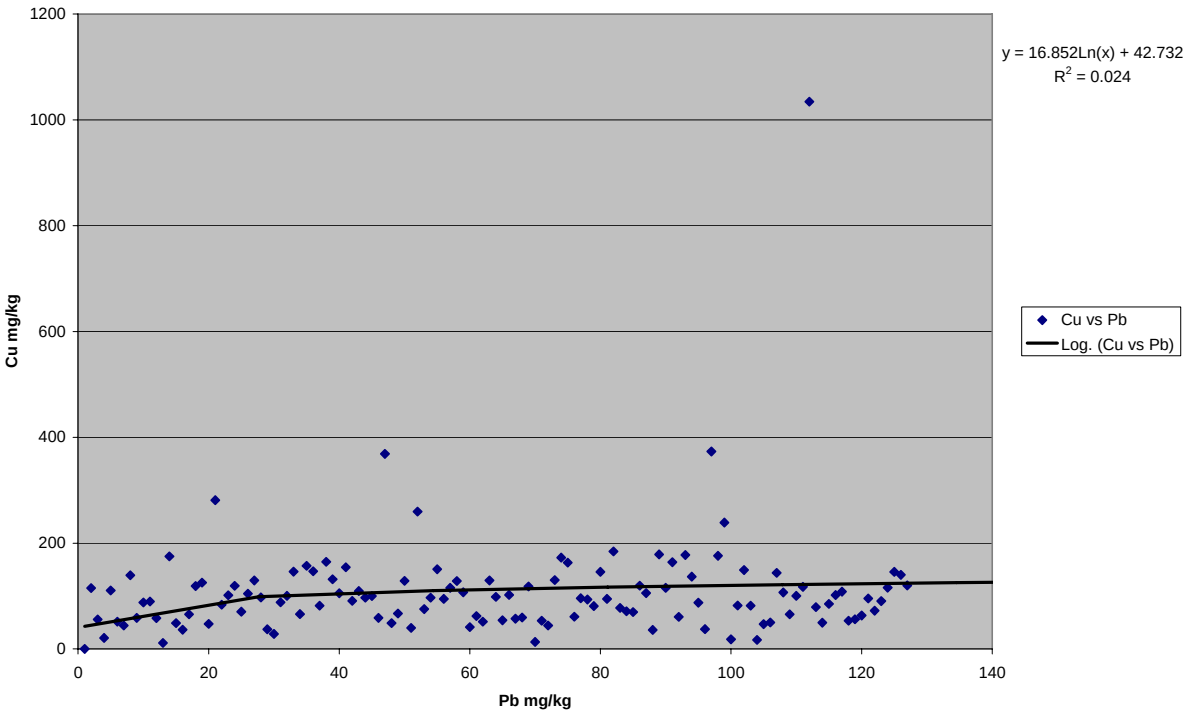


Figure 21 Pb vs Cu scatter plot

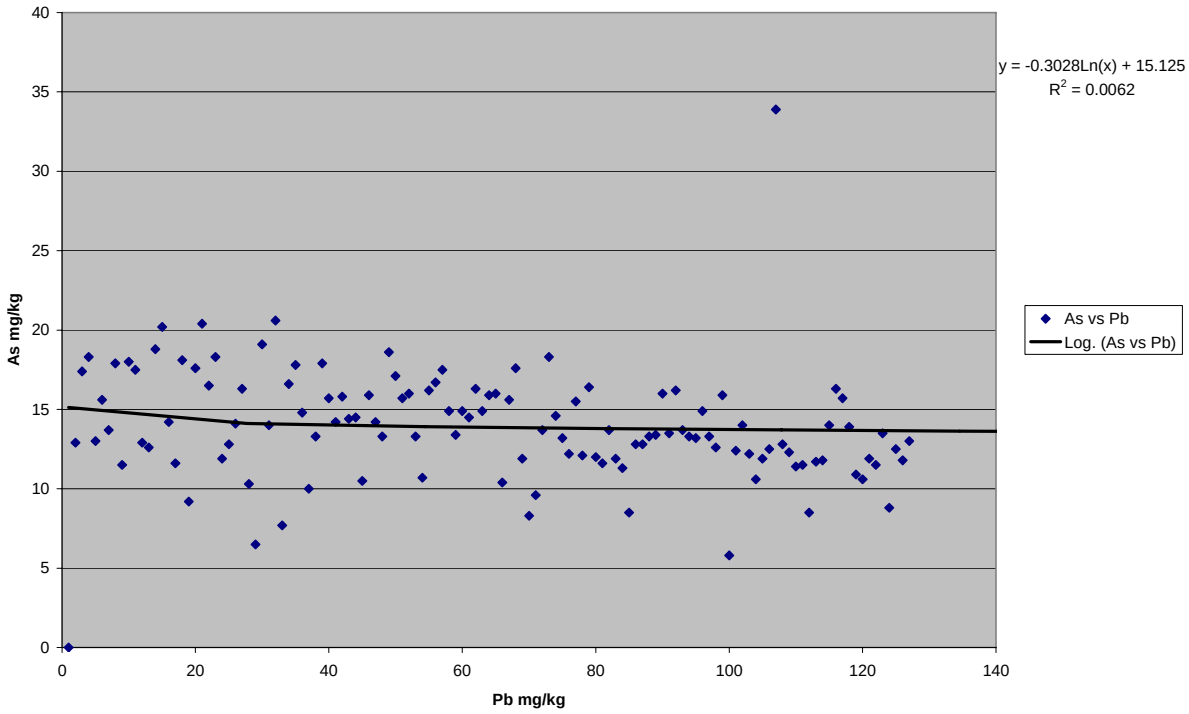


Figure 22 Pb vs As scatter plot

As exemple Pb vs Zn, Pb vs Cu and Pb vs As plot are shown. Is clear that Zn and Cd present positive correlation with Pb, while As has negative correlation and it is, probably, mostly geogenic...

Other elements (As, Sn, Tl, and Co) which were assumed to be mostly geogenic on the basis of their spatial distribution patterns have been plotted versus As.

While Tl and Co confirm the thesis of a geologic origin being positively correlated with As (Fig. 23), As-Sn scatter plot does not present a neat distribution of variable couples and the Sn origin in the Casoria territory appears to be dependent on both natural and anthropic sources (Fig. 24).

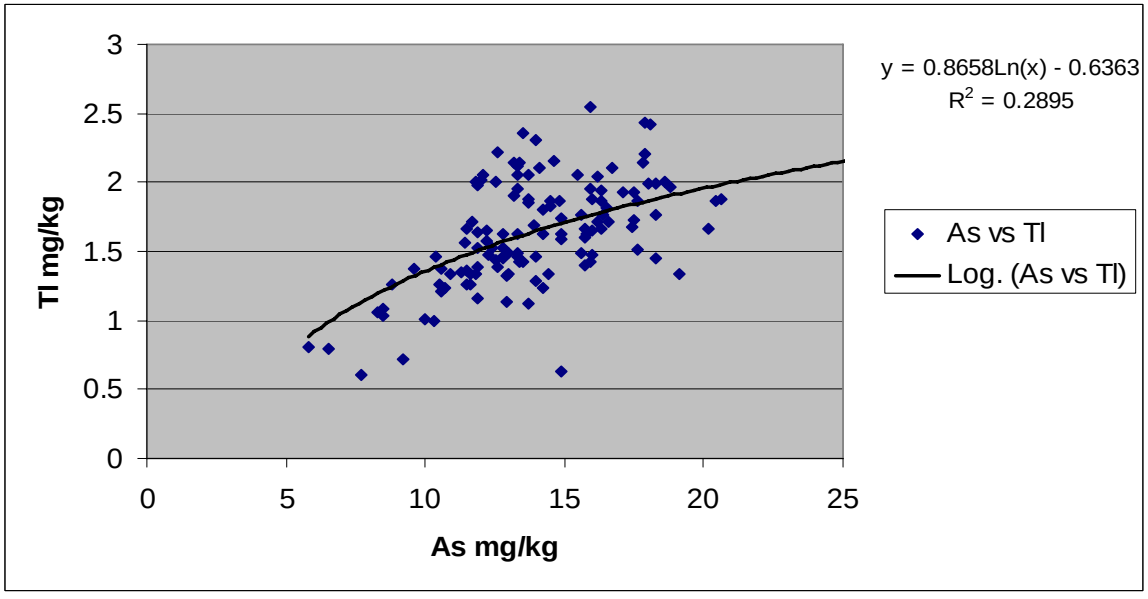


Figure 23 As vs Tl scatter plot

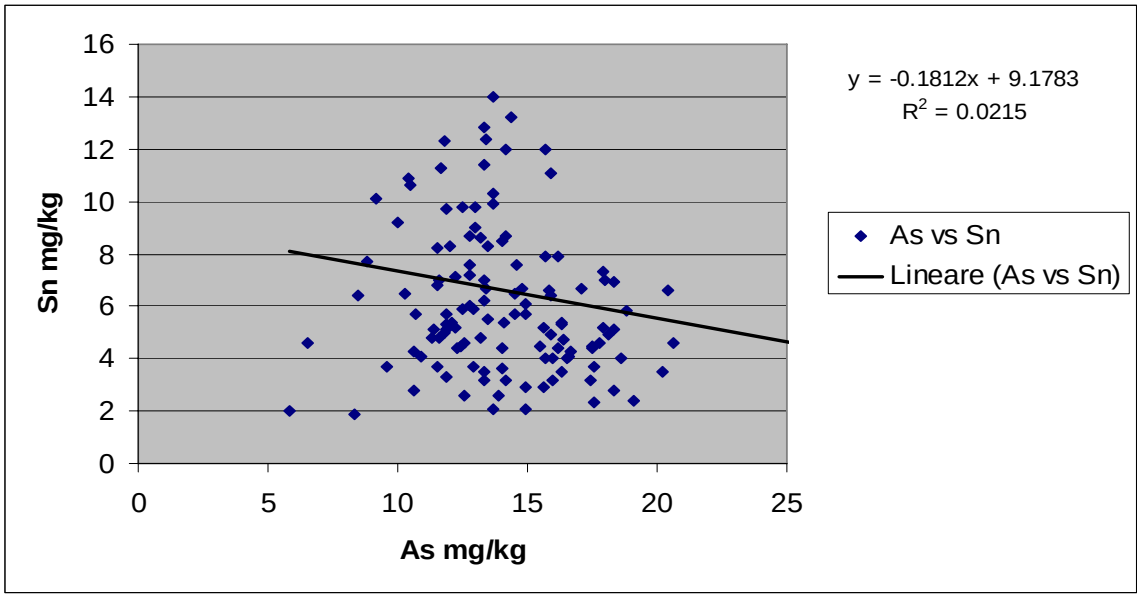


Figure 24 As vs Sn scatter plot

The degree of contamination due to potential harmful elements such as Pb, Zn, Cd needs to be quantified and spatially bounded to support ecological risk assessment (ERA) process..

In this work ***Contamination factor*** **(C^i_f)** has been calculated for each harmful element, also on a GIS basis, to evaluate the pressure on the urban/suburban environment of Casoria due to anthropic activities. and it expresses a potential ecological hazard of a given contaminant in relation with a given area (Hakanson, 1980).

The original formula to calculate the *Contamination factor* is as follows*:*

$$C_f^i = \frac{\overline{C}_{0-1}^i}{C_n^i}$$

Where C^i_{0-1} is the mean content of the substance *I* from at least 5 sample sites, and C^i_n is the pre-industrial reference level for the substance.

In a GIS environment (ArcView GIS 3.2), for each element evaluation of C^i_f has been obtained dividing the interpolated grid of elemental concentration by the background value of the element in Neapolitan volcanic soils (Cicchella et al., 2008) assumed as pre-industrial reference level.
The following terminologies have been used to describe the grade of contamination determined by means of C^i_f:

C^i_f <1, low contamination;
1≤ C^i_f <3, moderate contamination;
3≤ C^i_f <6, considerable contamination;
C^i_f ≥6, very high contamination.

Casoria shows moderate to very high level of contamination for Pb, Zn and Cd principally in the higher urbanized areas.

C_f^i observed for Cd shows considerable and very high values of contamination in the northern urbanized area, in the western area and in southern urbanized area of Arpino where a an intense potential ecological hazard cvan be assumed. (Fig. 25)

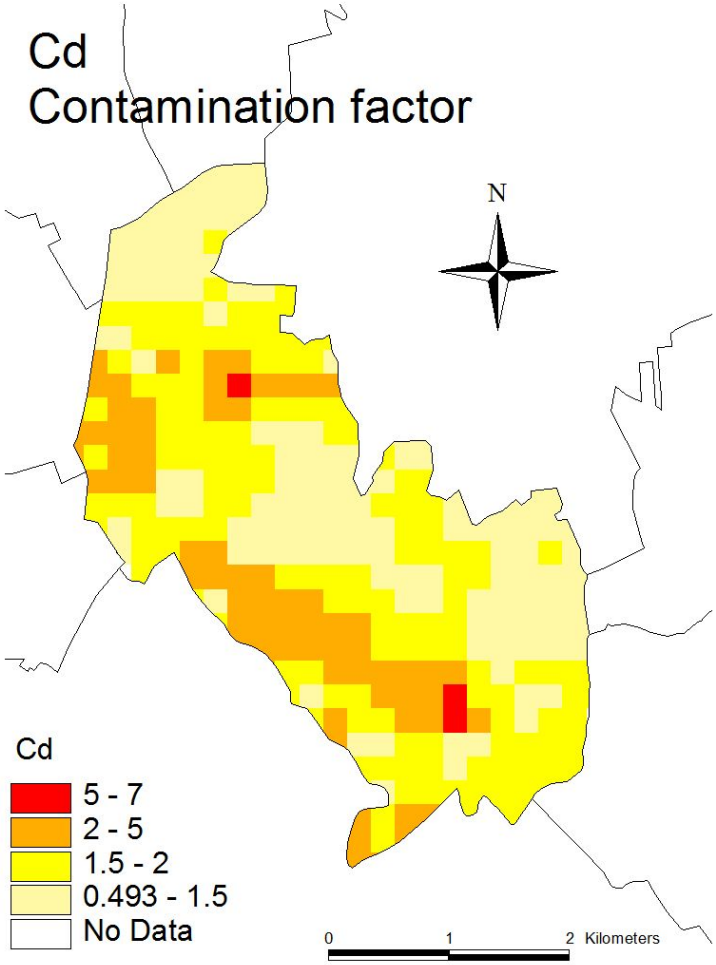


Figure 25 Cd contamination factor

Pb contamination factor shows the same spatial trend observed for Cd, but the higher hazard is found in the western area closed to city border of Naples.,(Figure 26)

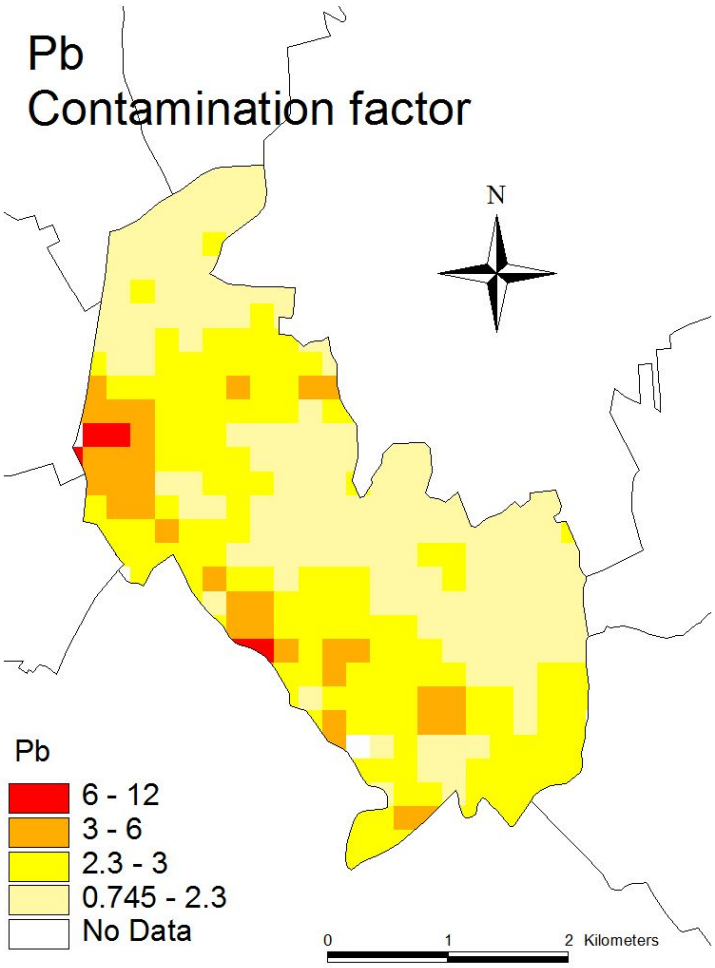


Figure 26 Pb contamination factor

Zn shows the same trend observed for the other element; the higher contamination factors have been found in the western areas and in the southern sector closed the highway. Moderate contamination is spatially widespread .(Figure 27).

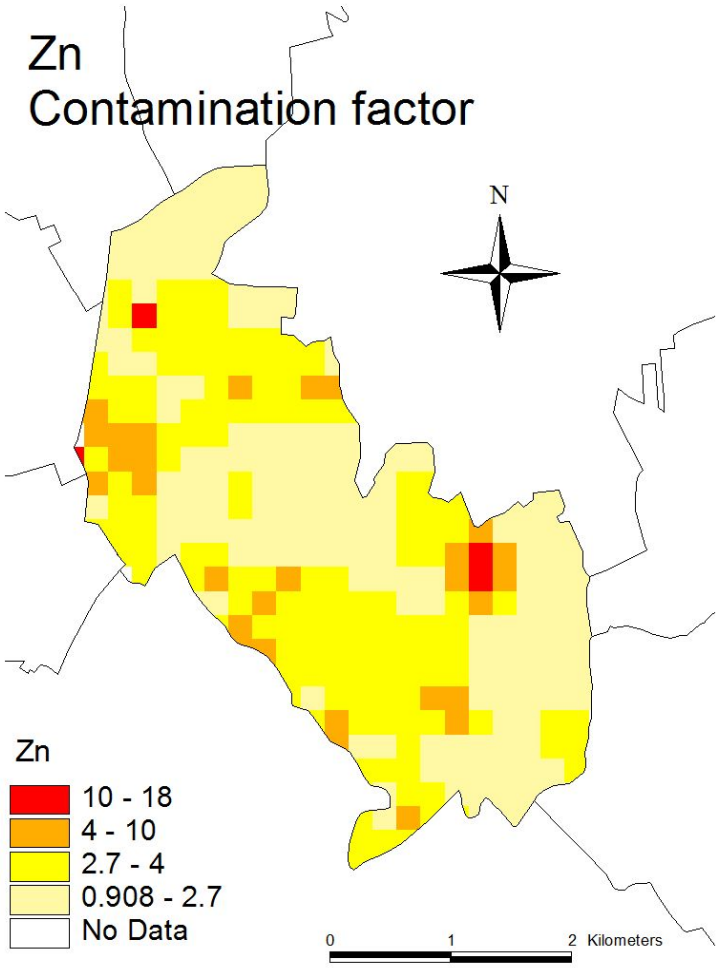


Figure 27 Zn contamination factor

The *total degree of contamination* (C_d), is the sum of all contamination factors (C_f) for a given area.

$$C_d = \sum_{i=1}^{8} C_f^i = \sum_{i=1}^{8} \frac{C_{0-1}^i}{C_n^i}.$$

With this approach, we have a contamination factor (C_f), which accounts for the contamination of single elements according to the concentration requirement, and a C_d-value, which accounts for the total of the sediment pollution within an area. Elements that should be considered are PCB, Hg, Cd, Pb, As, Cr, Cu, Zn (Hakanson ,1980)
In Comune di Casoria we consider only 3 elements who shows the higher anthropic influence.
The following terminology may be used to describe the degree of contamination (for 3 elements)
$C_d < 3$ = low degree of contamination:
$3 < C_d < 6$ = moderate degree of contamination;
$6 < C_d < 12$ = considerable degree of contamination;
$12 < C_d < 24$ = extreme degree of contamination;

The determined degrees of contamination ($C_{d)}$ (Figure 28) confirm that:

- Moderate to extreme degree of contamination characterize the urbanized areas with some extreme values in correspondence with the shared administrative boundary with Napoli..
- Hazard of potential health problems for the Casoria inhabitants in the higher urbanized areas is real.

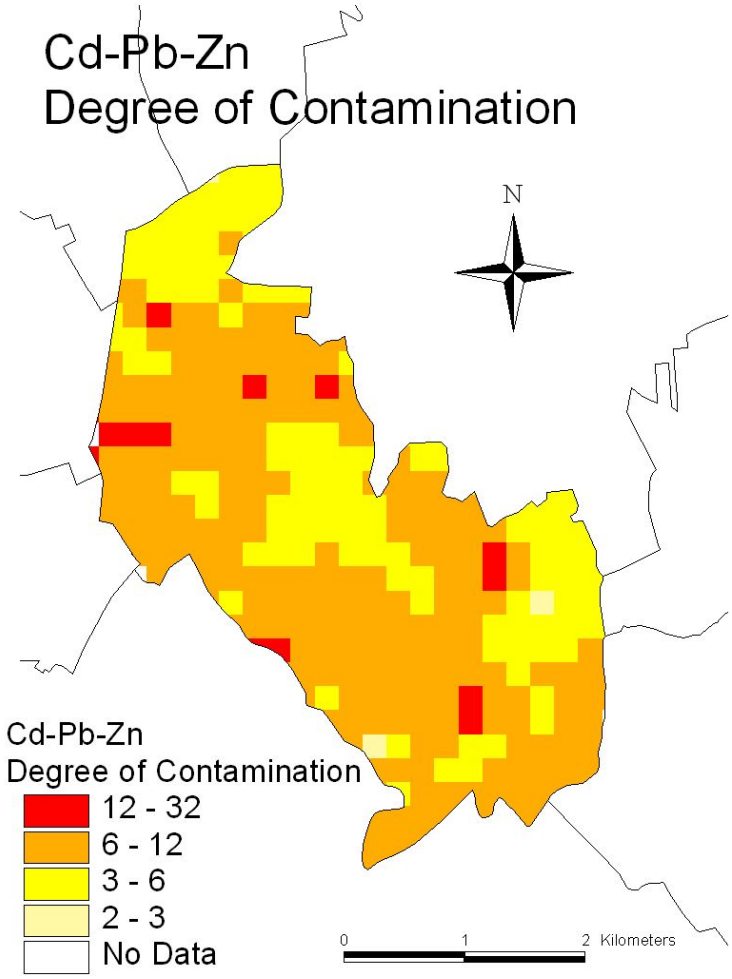


Figure 28 Cd-Pb-Zn degree of contamination

Heavy metal pollution in surface soils sampled in Comune di Casoria, exceed the intervention limits defined by the D.Lgs. 152/06 Italian Environmental Law for residential areas for Pb (100 mg/kg), Zn (150 mg/kg), Cu (120 mg/kg), Tl (1 mg/kg) and Be (2 mg/kg) in almost all the studied area; V, Hg and Ni concentration values are all below the residential limit;

As, Cd, Co, Cr, Sb concentrations are also below the residential limit, except for few samples.

About the Pb isotopic composition of surface soils and soil profiles there is an high correlation with industrial and incineration aerosol depositions. Lead gasoline used until 20 years ago probably has influenced Pb isotopic imprinting of Casoria soils. This is confirmed by previously isotopic studies on Neapolitan industrial settlement of Bagnoli (Tarzia et al. 2002), Neaples soils (Cicchella et al. 2008) and Agro Aversano - Litorale Domitio (Grezzi et al., 2010 and Bove et al., 2010) which overlays Casoria isotopic values

On the other hand one of the analyzed soil sample (CAS004) shows a high correlation with the local isotopic imprinting of the bedrock (Ayuso et al., 1998; D'Antonio et al., 1995), mainly characterized by, pyroclastites and other volcanics from the Vesuvius and Campi Flegrei.

CAS004 sampled in a northern field in which no contamination seems to be present, were analyzed to confirm the different trend showed by As-Pb plot (Fig. 10).

Soil profiles superficial level shows the same trend of surface soils: isotopic imprinting typical of Neapolitan urbanized and industrialized (ex-italsider) areas

Profile soils sampled on the bottom (depth 90-100 cm) shows a similar trend with Profile samples (0-10 cm); isotopic ratios overlaps each other but they follow a regular trend in which residues are shifted toward the geologic signature and leached are closer to the aerosol area.

Analyzed samples taken in the deep soil horizon, are mainly concentrated in the same field of surface soils, it is possible that the contamination is leached from the surface to the deepest level.

Finally it is possible to divide Casoria in two different isotopic fingerprint areas:

- one controlled by bedrock imprinting, with As high concentrations and Pb low concentrations, the latter mostly geogenic in the north side.
- one strongly influenced by anthropic activities in which potentially harmful heavy metals, such as Pb and Zn, concentrations are higher than in the rest of the territory.

These pronounced spatial correspondence between anthropic activities (vehicular traffic, industrial works, waste disposal and burning) and Pb, Zn, Cd higher values detected in the urbanized and industrialized areas, principally on the Naples border, and between geogenic sources and As higher values, are what we expected from the isotopic analysis.

This trend is confirmed by the different isotopic ratio between leached and residue: residues are shifted toward the geologic signature and leached are closer to the aerosol area.

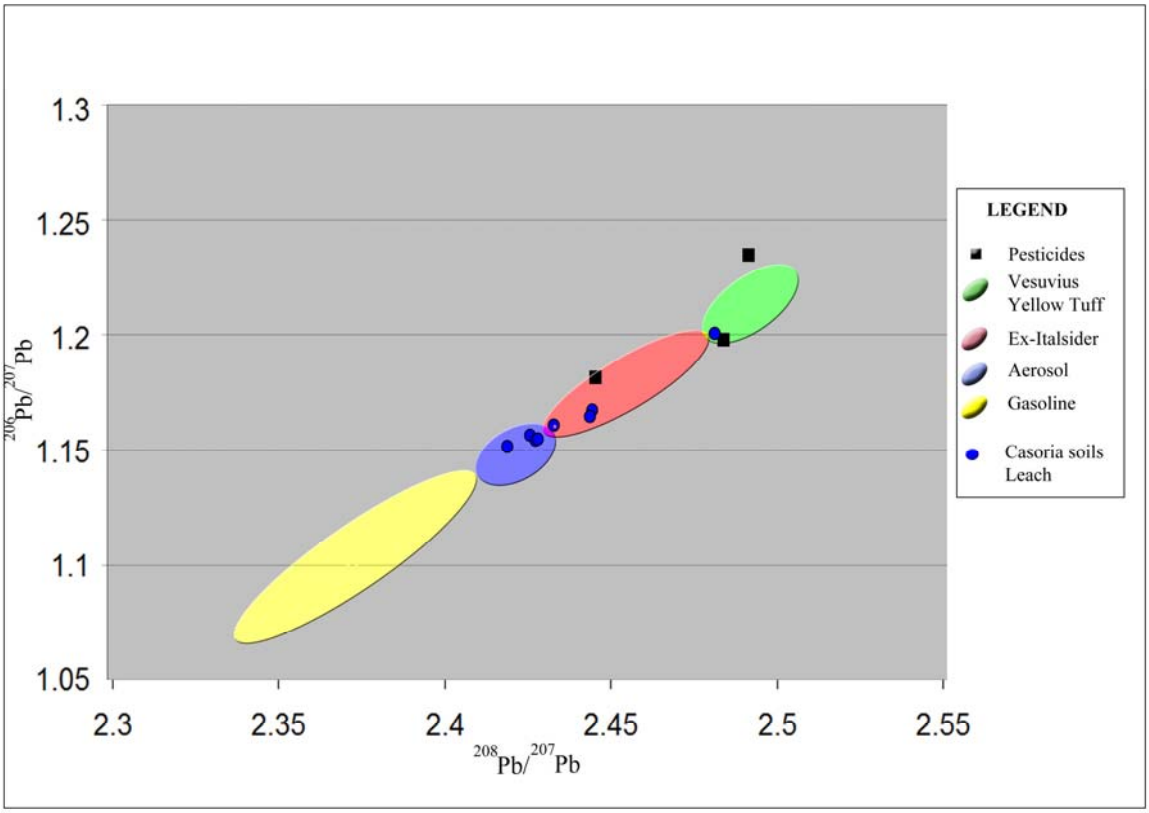


Figure 29 Casoria Surface soil isotopic ratio. Vesuvius (Ayuso et al. 1998), Yellow Tuff (D'Antonio et al. 2010), Ex Italsider (Tarzia et al.2002), Aerosol (Geagea et al 2008, Tommasini et al. 1999, Monna et al.1997) Gasoline (Monna et al. 1997, Chiaradia et al, 1999)

In conclusion, Casoria soils shows different levels of contamination due to anthropic activities (vehicular traffic, industrial works, waste disposal and burning) in accordance with previously works in Neapolitan Province and Campania Region (Agro Aversano and Domitio littoral). Is possible to affirm that Casoria is part of a seriously contaminated area which includes the highest urbanized and industrialized sites of Campania Region and the sites in which in the last 30 years illegal waste dumping were conduced (City of Naples, provincial northern area, and the National Interest Sites of Domitio littoral and Agro Aversano).

In particular:

- In the northern sector is possible to recognize 2 principal source of contamination:
    1. ex industrial settlements (Montefibre, ADS and Railway)
    2. high urbanized area and vehicular traffic
- In the western sector is possible to recognize 2 source of contamination:
    1. high urbanized area and vehicular traffic on the border with city of Naples
    2. International airport of Capodichino
- In the southern area is possible to recognize 2 source of contamination:
    1. high urbanized area (Frazione Arpino)
    2. vehicular traffic (Highway and via Nazionale delle Puglie)

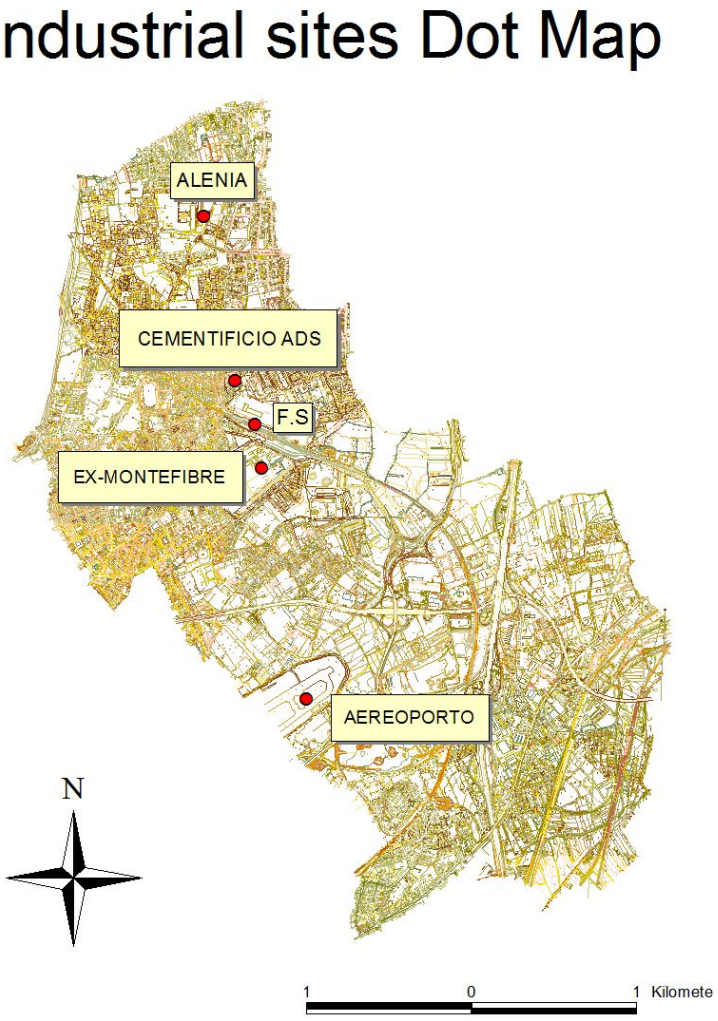


Figure 30 Principal industrial or ex industrial settlements sited in Comune di Casoria

Waste disposal and burning could be another source of contamination; but it is impossible locate and link directly high contamination sites with illegal waste disposal or burning sites.
Actually only few landfill sites has been mapped by authorities and is not yet clear what kind of waste has been disposed.

About the tap water, the results of this pilot study on the territory of the Comune di Casoria, suggest even more thorough surveys and studies, because of Pb isotopic results, extended on all the Neapolitan province territory and on Serino springs to detect the natural Pb isotopic ratio.

A more detailed study on tap water should be helpful, if this data will be confirmed, to find a direct source of potential risk for health due to many uses an way of bioavailability.

What is affirmed in this work will be further developed in an article collecting new geochemical data on profile soil samples and tap water. The aim of this article is to use Comune di Casoria results linked to previously article on Neapolitan area to quantify the anthropic component of contamination.

Particularly for tap water this is the first kind of study made in this area and no previously data has been available, only US Army during the last years conduced an analytical work on tap water in the US "sensible sites" in the Campania region and Neapolitan province. This study shows that in tap water potentially dangerous contaminant are present, but no data about source of this contamination has been carried out.

Actually safety procedure has been planned by US authorities in these areas; so this article on Comune di Casoria could be the fundamental tool to recognize, using isotopic data, anthropic source of contamination and to plan safety procedure on local and provincial scale seems to limit their bioavailability. Local authorities and international partners will be part of this plan using Casoria pilot data for further studies.

This study conduced on local scale can be also an important contribution to decision-making by local authorities to plan intervention aimed at the safety. For this reason in this work has been detected by Contamination Factor, Degree of Contamination an Italian D.Lgs.152/06 residential threshold, sites in which contamination is potentially dangerous.
Spatially it is possible to detect different areas in which anthropic pressure is higher:

- closer to Naples border and the International airport on the west side
- in the north-center sector due to the ex industrial settlements and the City of Casoria historical urbanized area
- in the southern sector due to the new urbanized area of Arpino, highways and via nazionale delle puglie.

The northern sector still remain less urbanized and this is demonstrated by high As values typical of Neapolitan background value, low heavy metals values, and confirmed by isotopic analysis on sample CAS004 which shows the same imprinting of Neapolitan volcanic bedrock.

High environmental risk made by Pb, Zn, Cd, Cu, Sn and Tl contamination which exceed D.Lgs 152/06 intervention limits in several areas of Comune di Casoria, needs to be processed by local and regional authorities to plan remediation activities.

Previously research that linked epidemiological and geochemical data in Campania Region (Albanese et al 2007) infact shows potential spatial connection between some neoplasm and relative high concentration of heavy metals.

So, Casoria inhabitants health risk made by this anomaly heavy metals concentrations will be carefully analyzed in a future article "Geochemistry and health: pollution from heavy metals and epidemiology in Comune di Casoria" trying to understand if exist a relation between environmental contamination and health risk.

In the last years environmental problems in the Campania region becomes on worldwide attention for different kind of reasons. The illegal disposal of domestic and other potential dangerous wastes and the burning of trash piles have raised concerns in the Naples and Caserta provincial areas that people who lives there could be at risk of unacceptable health consequences from exposure to the trash and related contaminants.

Actually epidemiological screening on Neapolitan and Casertan polluted areas were not produced by Italian authority, only available data will be carried out from "Atlante della Mortalita` della regione Campania" and from the pilot study made by WHO on epidemiological screening of Naples and Caserta provinces linked to waste crisis. This data, and several medical article shows in all the Neapolitan area Mortality Ratio higher than Italian level, which is possible to relate to potential harmful elements high concentration levels.

Isotopic data produced in this work can give a new work approach and will be useful to relate potential source of contamination detected (lead gasoline used, industrial and waste incineration aerosol), with high mortality ratio neoplasm.

In these last years epidemiological studies have been carried out in relation to landfills or incinerator settlements neighborhood, linking the potential level of contamination produced, to neoplasm or non-cancerous pathologies.

Unfortunately this studies report an increased risk of cancer and other diseases but no causal link has been so far adequately assessed.

Using gochemical and isotopic information will be possible to give further information and tools to determine if a causal link exist.

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